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Thermal Properties of Cryogen Frozen Foods and Changes Occurring at Sub-Zero Temperatures.

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ABSTRACT

Changes in the thermal properties of foods were measured at cryogenic temperatures produced by liquid nitrogen, and the qualities of foods cooled and frozen by this cryogen were evaluated.

Experimental evidence obtained from chemical, bacteriological, histological and organoleptic tests, showed that the use of liquid nitrogen as a cryogen for the preservation of foods resulted in superior products when compared to foods preserved by conventional methods of refrigeration. Comprehensive studies on shellfish showed that the shelf life of both shrimp and oysters was extended either (1) after rapidly freezing in liquid nitrogen, or (2) after using liquid nitrogen to maintain temperature for refrigeration of the products until brought ashore for processing.

It was necessary to measure the specific heat values of oysters and shrimp to determine accurately the volume of liquid nitrogen required to cool a given amount of product to a given temperature. The experimental values were compared to the specific heats obtained by computing the sum obtained by multiplying the heat capacity of each component of the food by its weight fraction. Knowledge of the specific heat is essential for developing mathematical equations for calculating cooling and thawing time.

The combination of the low boiling point -196°C (-320°F) and the high heat of vaporization (86 B.T.U./lb) of liquid nitrogen, plus the

fact that the gas absorbs about 80 B.T.U. per pound in going from its boiling point to 0°F, make liquid nitrogen an economical refrigerant. Another advantage is the fact that nitrogen expands 600-fold in its transformation from a liquid to a gas, and this cold gas constitutes an effective medium for cooling all parts of an enclosure.

I. INTRODUCTION

Freezing temperatures once feared by mankind, have been converted to his advantage by his continuing inquiry into this phenomina. While ice-salt systems were used to freeze foods in the mid 1800's, patents for freezing fish, for example, were granted to H. Benjamin in England in 1842, and later to Enoch Piper in Maine in 1861 (78). The invention of mechanical refrigeration in the later 1800's provided the basis for subsequent commercialization of the process. Frozen foods have become important items of commerce (90% of Iceland's export trade is frozen fish) and important food preparation for dinner table.

The advent of the process known as "Quick Freezing" has solved many of the problems involved in preserving fresh uncooked foods and also, those which require cooking, but not over cooking. By the process of quick freezing, fish, meat, poultry and vegetables may be preserved in a substantially raw, fresh state, for long periods. Many foods, precooked to a desired degree, may be preserved in the same manner. Quick frozen foods are those which are prepared ready for use and then packaged, labelled, and frozen in consumer sized units, which remain unopened and solidly frozen until purchased by the ultimate consumer.

It cannot be stated that any one individual in particular invented the process of ultra-rapid freezing which is the basis of quick freezing.

In the late 1920's, scientiests and food technicians all over the world, and especially in Canada, were studying methods of rapid freezing, and even the possibilities of sub-dividing the larger pieces of food so that they could be more easily frozen and packaged. There is no doubt, however, that it was Clarence Birdseye (83), who first tied all the different facets together and created quick freezing as a composite and commercial form of food processing. Birdseye also invented a first class freezing machine which he called 'frozener' and which in a modernized, but not greatly altered form, in use today.

Clarence Birdseye, and the original Birdseye Laboratories in Gloucester, Mass., deserve a great deal of credit for the introduction of this merchandizing system in the United States. This method involved the following systems:

(1) The selection of strictly fresh foods of the best quality;

(2) The preparation of the food for the table;

(3) The treatment of the product so as to prevent deterioration during storage;

(4) The compact packaging of the food in moisture-vapor proof, substantially air-tight packages;

(5) The rapid freezing of the packaged food;

(6) The storage of the food at 0°F or below for not longer than twelve months;

(7) The merchandizing of the solidly frozen product from retail display cases in which it was held at 0°F; and

(8) Suggesting to the housewife that she hold the product solidly frozen until several hours before it was cooked.

From the above eight points, it is obvious that quick freezing is only one of the equally important steps. Without the other seven steps, the system probably would fail.

The advantages of quick freezing over slow freezing of foods may be summarized as follows:

(1) The ice crystals formed are much smaller, and therefore cause considerably less damage to the cells.

(2) Less time is allowed for the diffusion of salts, and the separation of water in the form of ice, because the freezing period is much shorter.

(3) Since the product is rapidly cooled down to the freezing point, oxidation and other undesirable changes are held a minimum.

(4) The product is quickly cooled below the temperatures at which bacterial, mold, and yeast growth occur, thus preventing decomposition during freezing.

(5) A highly practical reason in favor of quick freezing over slow freezing is the inherent speed and capacity of these methods for commercial processing plants.

The anticipated dollar growth rate of major food categories for the period 1960-1975 with annual percentage increase is presented in Table I.

TABLE I

Anticipated Dollar Growth Rate of Major Food Categories 1960-1975 with Annual % Increase (4)

Product Category	Billion of 1960 Dollars				Annual Rate of Growth (1960-1975)
	1960	1965	1970	1975	
Meat Products	20.5	23.6	26.9	31.1	2.8
Dairy Products	12.9	14.2	15.4	16.6	1.7
Poultry and Eggs	6.6	7.1	7.3	7.7	1.0
Bakery and Cereal Products	9.5	10.4	11.2	12.1	1.6
Fruit and Vegetables	14.7	16.5	18.5	20.7	2.3
Other Foods	6.6	8.2	10.1	12.2	4.2
Meals Away From Home	12.0	14.1	16.2	18.8	3.0
TOTAL	82.8	94.1	105.6	119.2	2.5

II. REVIEW OF LITERATURE

Thermal Properties of Foods at Cryogenic Temperatures

The determination of refrigeration load for a freezing or storage plant is dependent on several factors. It is on the basis of the calculated load that plans may be made for specific machines and equipment to supply the necessary refrigerating capacity.

In the freezing or storage of foods at low temperatures these operations take place within an insulated space. Insulation is only the physical barrier which reduces the transfer of heat from the relatively high temperature area surrounding the freezer to the low temperature area within. The number of B.T.U. per hour passing through one square foot of wall surface, one inch thick, for each degree Fahreinheit difference in temperature, between the two sides of the wall, is known as the 'Thermal conductivity' of the insulation material (K).

The specific heat of foods is required in calculating the refrigeration load. Knowledge of the specific heat is also needed for calculating cooling and thawing time. Consequently, the specific heat of a substance can be defined as the ratio of the heat required to raise the temperature of unit mass of the substance by one degree, to the heat required to raise the temperature of an equal unit mass of water by one degree. The specific heat of a food material when the temperature is above freezing is the quantity of heat in B.T.U. that

must be removed to reduce the temperature of one pound of the product 1°F. The specific heat after freezing is the quantity of heat in B.T.U. which must be removed to reduce the temperature of one pound of product by 1°F to the storage or the final temperature. The latent heat of fusion is that quantity of heat in B.T.U. which must be removed to cause a change of state at the freezing point for one pound of the product (from unfrozen to frozen at 28°F). Table II shows the specific heat and latent heat per pound for a number of foods.

The product load is the quantity of heat which is to be removed from the product being stored or frozen, so as to reduce the temperature of the product from its initial temperature to that temperature consistent with the practice of frozen foods. The product load can be calculated by the following formula:

$$H_3 = (P)(h_b + h_{1f} + h_a)$$

where

H_3 = product load in B.T.U.

P = pounds of product

h_b = B.T.U. per pound necessary to remove to cool from initial temperature to the freezing point (usually 28°F)

= (specific heat)$(t_1 - 28°F)$

h_{1f} = latent heat of fusion of product, B.T.U. per pound

h_a = B.T.U. per pound necessary to remove to cool from the freezing point (28°F) to the storage temperatures

= (specific heat)$(28°F - t_2)$

TABLE II

Specific Heat of Foods (B.T.U./Lb) (77)

Food	Above Freezing	Below Freezing	Latent Heat of Fusion, B.T.U./Lb
Fish, Fresh	0.76	0.41	101
Oysters	0.90	0.46	125
Bacon	0.55	9.31	30
Beef	0.66	0.38	94
Pork	0.60	0.38	66
Poultry	0.80	0.41	99
Apples	0.89	0.46	125
Peas	0.80	0.42	108
Milk	0.90	0.46	124
Butter	0.30	0.24	18

The refrigeration load is the sum of the following:

1. Wall losses
2. Air change losses
3. Product load
4. Miscellaneous losses

Before 1942, most available information on the specific heat of foods was based on the work of Siebel (77). He reasoned that since foods were composed of water and solid matter, it should be possible to calculate their specific heat above the freezing point by adding the product of the weight fraction of water present, and its specific heat, to the product of the weight fraction of the solid matter, and a constant 0.2, as its specific heat. Below the freezing point he used only the specific heat of ice. Manheim et al. (57) in their studies of enthalpies involved in food freezing concluded that the exact moisture content of the specific food must be known in order to calculate its specific heat. An incorrect moisture content can be a source of considerable error in commercial calculations.

Short et al. (76) measured the specific heats of some fruits, vegetables, meats, and sugar solutions, and found that the assumption of Siebel was not correct, especially in the region between 115°C (+5°F) and 4.4°C (+40°F). In the region below -15°C, Short et al. stated that the numerical values are roughly the same as would be obtained by averaging the specific heat of ice and the solid matter.

Working on the development of a rapid method for continuous determination of the specific heat of foods over a wide range of

temperatures below the freezing point, Moline et al., (57) determined the specific heats of fats, gelatin, and water. They suggest from their data, that it is possible to estimate the specific heat of foods based on their composition, and using an appropriate correction factor. They explained the discrepancies between the observed and the computed specific heat values for meats and fish, as due to the vitreous ice formation when the samples are frozen. Tables III and IV show the specific heat of a model system used by them, and was obtained by direct measurement. This can be compared with Table IV, which was computed by constituent analyses.

Short and co-workers (76) decided to determine what relationship, if any, existed between heat capacity and the composition of food stuffs. The lower temperature of his bomb calorimeter was -40°C. The foods used during his experiments were fruits and vegetables. He was unable to measure the specific heat of any food containing more than 3 percent fat, because kerosene was used as the heat transfer medium in the calorimeter. Kerosene dissolved the fat to form a thick jelly that could not be stirred readily. He also found that his data did not follow Siebel's rule between -40°C and +5°C.

Using an adiabatic calorimeter, measurements of enthalpy and specific heat, and calculations of ice portion (kilogram of ice per kilogram of total water content) were made on the temperature range of -40°C to +20°C were tabulated. Experiments with predried fish flesh indicated that even at very low temperatures, the non-freezing water

TABLE III

Specific Heat Values of Ice, Fats, Protein (Gelatin), Used to Calculate the Specific Heat of Food Stuffs (57)

Sample	-40°C	-80°C	-120°C	-160°C
Ice[a]	0.438	0.368	0.298	0.232
Gelatin[a]	0.310	0.250	0.201	0.151
Beef Fat[a]	0.550	0.371	0.239	0.202
Lard[a]	0.383	0.290	0.245	0.211
Butter[a]	0.465	0.322	0.264	0.240
Sodium Chloride[b]	0.194	0.185	0.171	0.149
Dextrose[b]	0.230	0.184	0.139	0.112

[a]Values obtained by experiment.

[b]These values were obtained from International Critical Tables.

TABLE IV

The Specific Heat of a Model System[a] as Obtained by Direct Measurement Compared to the Specific Heat Calculated by Constituent Analysis (57)

	C_p		
°C	Computed[b]	Observed	Observed/Computed
-40	0.435	0.468	1.07
-80	0.348	0.387	1.11
-120	0.271	0.307	1.13
-160	0.212	0.228	1.13
		Av.	1.11 ± 0.03

[a]Composition of the model system was 64.4% water, 17.6% protein, and 18.0% fat.

[b]The sum obtained after multiplying the specific heat of each component by the weight fraction present.

portion was largely independent of the initial water content. At high water content, this portion remained unchanged during freezing. Included in this work are data on the percentage of frozen water as a function of temperature and initial water content (Riedel, 72, 73).

Riedel (74) continuing his earlier experiments with fish, measured the enthalpy of lean beef in the temperature range of -60°C to +20°C. He used an adiabatic calorimeter, at different water contents, and determined the portion of the water frozen at each stage. He observed that even at very low temperatures, the more freezing portion was about 0.35 kilogram per kilogram of dry matter; and this corresponded to 0.4 kilogram of water per kilogram of protein, or 2 molecules of water per amino acid residue of the protein.

Jason et al. (43), using an adiabatic calorimeter, determined the apparent specific heat of cod muscles in the temperature range of -70°C to +0°C. They obtained the temperature of the sample as a continuous function of the heat in-put and the apparent specific heat by graphical differentiation of the heat content curve with respect to temperature.

The heat capacity of gelatin-water mixture with gelatin concentrations of 9 to 100 percent over the mixtures between +25°C and -180°C was measured in an adiabatic calorimeter (Hampton and Mennie, 57), previously used by other workers (Barnes and Maass, 5). However, it is impossible to obtain accurate specific heat values from these data.

Other authors (Tressler and Evers, 83) have listed specific heat values for foods above and below freezing points, but did not define the temperature range of these measurements.

The Effect of Cryogenic Temperatures on the Biochemistry and Bacteriology of Shellfish Deterioration

Shrimp: Shellfish, both crustacea and mollusca, are subject to types of microbial spoilage similar to those for fish. Many pertinent publications are available which summarize such classes of bacteria present shellfish, but only a few convey sufficient information as to cultural characteristics and strain differentiation. This lack of thorough identification makes comparison of research data very difficult. Deterioration of shellfish quality is considered generally to result from the action of enzymes from both the tissue and the contaminating microorganisms originally present on the shellfish, or introduced during catching, handling, and processing. Spoilage of the product is believed to be mainly the result of the bacterial action, and is caused by the consequent formation of compounds which impart off-odors, color changes, and off-flavors. A comprehensive survey of literature reveals a lack of correlation between the types of bacteria and their numbers, and the induced chemical changes and their relationship to changes in quality.

The prevention of deterioration in the quality of shrimp involves two distinct problems, namely, maintaining low numbers of detrimental microorganisms, and the control of oxidations, chiefly of phenols into melanins. This reaction is guided by specific tissue enzymes --

phenolases -- and results in the appearance of black zones or spots at the edges of the shell segments of the flesh (Fieger and Bailey, 16, 18).

This dark color is produced by melanin pigments which form on the internal shell surfaces, or in advanced stages, on the underlying shrimp meat (Faulkner et al., 14). These pigments are produced by an oxidative process of tyrosinase on tyrosine. The reaction is accelerated by copper and other metalic ions (Fieger and Bailey 18).

Limited research has been reported on the numbers or kinds of bacteria found on fresh shrimp. Clark and MacNaughton (12) stated that the heads should be removed from freshly caught shrimp, which would then be washed and iced as quickly as possible, since the dark liquid in the stomach contains partially digested plant and animal material which readily decomposes. They stressed that this liquid and the surface slime must be removed by thorough washing before packing in ice. Cameron and Williams (10) investigated procedures in shrimp canning which would eliminate spoilage. They did not report the bacterial counts or the species isolated, but found that washed raw shrimp in canneries were heavily contaminated with bacteria. The practice of washing in tanks was inefficient because the water was not changed often enough, and sometimes the bacterial load on fresh shrimp was actually increased by washing. They recommended flume washing, and other sanitary precautions which would prevent spoilage in canned shrimp.

Numerous papers on the bacteriology of fresh-fishery products were reviewed by Griffiths (32). Green (30) showed that whole shrimp examined

immediately after emptying of the trawler net varied in bacterial counts from 1,600 to 1,200,000 per gram. The latter count was from shrimp caught in Barataria Bay, Louisiana, a shallow inland which receives drainage from the settled areas adjacent to the West bank of the Mississippi river. A more representative bacterial count of shrimp caught in commercial fishing nets in widely scattered areas in the open Gulf of Mexico off the Louisiana Coast found to be 42,000 bacteria per gram for 14 different samples. Green showed that an inverse correlation existed between the size of the shrimp and the bacterial count, and that higher counts (350,000) were obtained on shrimp caught in the test net than the count of 76,000 on shrimp caught in the same area in a regular net. This may be the result of longer time involved in regular trawling, which provided more adequate washing than the short time in which a test was made. One sample of mud taken in eight fathoms of water in the open Gulf contained 4,000 bacteria per gram, while surface water from the same location contained 25 bacteria per millimeter. Williams et al. (85) contend that the presence of mud on shrimp causes high counts.

When whole or headless shrimp from the same catch were washed with Gulf of Mexico water, there was an average reduction in the bacterial count (Green, 31). Bacterial counts on headless, unwashed shrimp were somewhat lower than the whole shrimp from the same catch. Removal of the heads in all cases reduced the count somewhat, the heads carrying approximately 75 percent of the bacteria (Fieger, Fieger et al., 16, 18).

The bacterial counts of freshly caught headless shrimp are largely determined by the bacteria and debris adhering to the surface. The average bacterial count on the shrimp as prepared for icying under commercial conditions, headed and washed by the fisherman, was 7,400 per gram. So it is evident that under commercial conditions, with expeditious handling and thorough washing, headless shrimp may be placed in ice storage on board trawlers, and carry a relatively low microbial load.

Since the melting ice from the upper layers of shrimp washes down over the lower layers, Green (31) also studied the influence of position in the bin on the bacterial counts. After 9 days storage, headless shrimp in the layer next to the top increased from 1,800 bacteria per gram to 2,400 per gram, whereas the bacteria in the bottom layer increased a thousandfold. Studies by Williams (84), Williams et al. (85), and Williams and Rees (83) complement those of Green in that they determined the types of bacteria initially present in fresh Gulf of Mexico shrimp caught adjacent to the Texas coast. They showed the main groups present were Achromobacter, Bacillus, Micrococcus, and Pseudomonas. These four groups made up 78 percent of the 1,200 isolates. In the biochemical characteristics they found 62 percent of the isolates were proteolytic, 35 percent lipolytic, 18 percent reduced trimethylamine oxide, and 12 percent formed indole. They failed to find any indication of a difference in bacterial flora between Penaeus setiferus and Penaeus duorarum.

When shrimp are stored without direct contact with ice, low bacterial counts result if the shrimp are handled carefully and expeditiously, but black spot becomes a severe problem (Green, 30). Later, Fieger et al. (18), further investigated this type of storage using the antibiotic CTC (chlorotetracycline), and such antioxidant dips as sodium bisulfite, ascorbic acid, and citric acid either separately or in combination. The CTC dips were effective in maintaining low bacterial counts through 15 to 20 days. The dips not containing CTC reduced bacterial counts insignificantly.

It has been established by several investigators that some bacteria are destroyed by freezing and during frozen storage. Literature describing the speed with which these bacteria are destroyed are controversial. Haines (34) found that various freezing temperatures produced essentially the same reduction in suspensions of bacteria, but that prolonged storage at various temperatures resulted in the greatest death rate at the higher temperatures, -2°C (28°F) being the most destructive. Weiser and Osterud (84), in extensive investigations, concluded that death by freezing involved a rapidly acting or "immediate" death, caused by freezing and thawing per se, and a "storage death" which is a direct function of time and temperature. They also concluded that death by freezing was marked, but did not vary with the intensity of the freezing temperature. They noted that repeated fluctuations of temperature below freezing did not exert a lethal action in addition to that of storage.

Prescott, Bates and Highlands (69) reported that bacteria in commercially quick frozen haddock, did not decrease in number during 25 weeks. They found that the bacterial count in a similarly frozen sample of lamb chops was reduced slightly, the greatest decrease occuring at -6.6°C (21°F). The best methods of freezing, packaging, and storing headless shrimp were investigated Fieger et al. (23). Waxed cartons overwrapped with glassine and heat-sealed were used. This was compared with regular glazing. Freezing took place at -40°F, and storage temperatures were -40°F, 0°F, 10°F, and fluctuating between 0°F and 10°F. Definite evidence of deterioration was noted in those samples stored for three months at 10°F, and at ten months, they were judged unacceptable. The samples stored at -40°F, had the appearance of freshly frozen shrimp, and were of excellent quality at the end of the storage period. Those stored at 0°F, but superior to those held at fluctuating temperatures. No significant differences were shown between the glazed samples and those having the glassine overwrap. Temperatures above 0°F cannot be recommended for storage of frozen shrimp. Bacteriological studies of these samples were reported by Holmes and McCleskey (38). The major problem in keeping and packaging frozen shrimp undoubtedly is the gradual drying of the product with ensuing chemical changes (Peters and McLane, 64). Peeled shrimp had lower bacterial counts than unpeeled shrimp. Storage at 10°F gave a lower survival rate than for those kept at -40°F.

A radical way to avoid microbial deterioration of the raw material is freezing at sea. Crowther (10) reported preliminary results using brine (calcium chloride, 40 percent by weight) at a temperature of -3°F. Similar trials were conducted in 1952 on both white shrimp (P.setiferes) and brown shrimp (P.aztecus) on board. Both brine and air freezing were tested during exploratory trips in the Mexican Gulf (Dassow, 13). A circulatory 85° salometer, brine chilled to 5°F was used for brine freezing.

Cultivation, processing, and packing procedures for market subject oysters to many potential sources of microbiological contamination. Therefore, thorough and constant control must be maintained to insure ultimate consumers of receiving a safe and edible product. A survey of literature offers considerable information concerning the nature of the problems involved.

Oyster: Areas designated for oyster cultivation usually present infinite possibilities of chemical, biological, and physical changes which contribute to a favorable environment for microbial growth. Changes in rate of flow of water in the area, weather variations, industrial developments, concentration of pollutants, and availability of nutrients for food are but a few factors contributing to the problem. Since such variable circumstances exist over short periods of time, innumerable strains of bacteria and yeasts will find suitable conditions for growth during the life time of any given oyster. Strict enforcement

of regulations is necessary therefore, to prevent the oyster industry from becoming a health hazzard.

Hunter and Linden (37, 38) showed that no relationship existed between the total number of aerobic bacteria present and the conditions of the oyster. They theorized that spoilage of oysters depends upon the presence and development of bacteria of certain types of groups, rather than the total number of organisms present, particularly those causing fermentation or putrefaction.

Decomposition of shucked oysters at the start is due to activities of some members of the Serratia, Pseudononas, Proteus, Clostridium, Bacillus, Aerobacter, and Escherichis group of bacteria. Later in the course of spoilage, Streptococci, Lactobacilli, and yeast find more suitable conditions for growth. A comprehensive survey of E.coli in market oysters was made by Tonney and White (82). Perry and Bayliss (62) ascertained the value of E.coli as an indicator of significant fecal pollution. Tanikawa (81) in an extensive study established the existance of a specific Coliflora in the intestines of Japanese oysters, readily distinguishable from any human origin.

Apparently, the role of yeasts in oyster decomposition has not received sufficient attention, even though all available evidence indicates these organisms to be a problem in the oyster industry. Hunter (35) found a pink yeast to be responsible for spoilage of oysters during shipment. A Torula yeast was isolated which grew readily at low temperatures, and was present in surface and bottom water of New England

beds. Although the yeast was found on normal oysters, the major source of contamination was found to be packing house equipment. Pink yeasts were isolated from frozen oysters held at temperatures between 0°F and -35°F (McCormack, 53). Furthermore, it was discovered by McCormack (54) that this pink yeast produces spores, and this greatly increases the risk of deterioration from this microorganism. A brown discoloration quite common in Gulf oysters is of an intrinsic and biochemical nature, has no relationship to any microbial activity (Fingerman, 24).

Almost every reported investigation of oyster spoilage has been made with fresh or frozen oysters in which the spoilage was of the fermentative type, characterized by a sour odor, or putrefactive in nature. Baldwin et al. (7) measured the changes in pH, water-soluble and alcohol-soluble nitrogen, and total titratable acidity during storage of raw Eastern oysters. From the standpoint of ease, rapidity, reliability of measurements as an indicator of oyster freshness, pH values seemed to them to be the most promising of these measurements. They described oysters at a pH of 6.2 to 5.9 as being in good condition, at pH 5.8 in an 'off' condition, at pH 5.7 to 5.5 in musty condition, and at pH 5.2 and below as sour or putrid. Similar findings were reported by Hunter and Linden (36), Piskur (66) and Pottiner (69), all of whom used changes in pH and organoleptic ratings as the criteria for judging the quality of raw oysters.

In Gulf oysters, the drop in pH is not necessarily correlated with the sour odor. The seasonal variation in pH, initially and at intervals

during subsequent storage at 41°F (5°C) was observed, with the values being lowest during the summer and highest during the winter (Gardner and Watts, 26).

The degree of washing and quality of water also influences the course of decomposition. A thorough clean-water washing seems to remove putrefying agents, leaving such microorganisms as favor fermentation and souring to dominate the subsequent deterioration (King et al., 44). Apparently, acids are formed from the breakdown of glycogen, known to be due to bacterial action or glycolytic enzymes, or both together, within the oyster tissue. In a basic study of glycolysis in the oyster adductor muscle, Humphry (40) demonstrated a relatively slow production lactic and pyrucic acids in tissue homogenates. Glycolytic activity in the oyster muscle proceeds at a much slower rate than in mammalian muscle, where all available glycogen is converted into lactic acid within a few hours under anaerobic conditions, which develop inside the tissues following slaughter. Apparently, no investigation has been made of glycolytic systems in other oyster tissues, although Hatanaka (34) found that most of the glycogen is in the soft tissue.

This formation of acids naturally has an effect on the development of the bacterial flora and might explain seasonal differences in the keeping quality of oysters. For Gulf oysters, a peak in carbohydrates is obtained in May and a minimum in August (Lee and Pepper, 47). A clear distinction is not always made between pH changes and other biochemical differences as they manifest themselves in still-living

oysters as compared to those taking place in dead specimens, whether in the shell or shucked. Gardner and Watts (26) were able to establish large seasonal differences as to the initial pH when Gulf oysters were harvested.

Hunter and Harrison (37) stated in shucked oysters stored at temperatures below 10°C (50°F) no multiplication of E.coli or other lactose-fermenting bacteria occurs. Tonney and White (82), on the other hand, reported that E.coli did multiply at 5 to 8°C (41-46°F). Wilson and McCleskey (86) could not confirm this, but found that Coliform organisms readily developed when shucked oysters were stored at 4-6°C (39-43°F). Initially, the increase was slow, but enormous numbers were encountered after 3 to 4 weeks. E.coli did not multiply and usually decreased during refrigerated storage. The entercocci usually remained unchanged for about two weeks, and often increased after 3 to 4 weeks. Consequently, E.coli appears to be a better indicator of pollution in stored oysters than either the coliform group or the enterococci.

The best initial means of retarding bacterial spoilage and avoiding associated dangers is to minimize the degree of contamination in processing areas and maintain careful sanitation during the preparation. Experimental results also indicate that rapid cooling and low temperatures, as close to 32°F as possible, will appreciably prolong the storage life. Slow cooling and higher storage temperatures are conductive to rapid spoilage (Liebman et al., 48).

It is apparent from the review of literature that foodstuffs can be preserved with improved product quality using liquid nitrogen. Shellfish (shrimp and oysters) are an important food because of their high nutritive value and palatability. As an article of commerce of the State of Louisiana and as a source of income, the shrimp industry is a major business. Nearly 70 percent of the annual United States catch of 150,000,000 pounds netting $10,000,000 comes from Louisiana water around the mouth of Mississippi. The annual loss of shrimp because of spoilage from the time caught until ready for shipment to remote markets is often as high as 20 percent of the total catch. In addition to this loss, some of the marketable shrimp are inferior in quality. Due to the characteristic of the product and the conditions under which it is caught, some loss is inevitable but the losses should and can be reduced considerably below the present level.

Table V shows the total supply of shrimp in the United States (1952-1962) and the nutrition value of shrimp are presented in Tables VI, VII and VIII.

TABLE V

Total Supply of Shrimp in the United States (1952-1962) (5)

	United States Catch			Imports		Total
Year	Heads-on, Thousand Pounds	Heads-off, Thousand Pounds	% Total	Heads-off, Thousand Pounds	% Total	Heads-off, Thousand Pounds
1952	227,221	135,251	78	38,471	22	173,722
1953	260,357	154,974	78	43,100	22	198,074
1954	268,334	159,723	79	41,519	21	201,242
1955	244,335	145,438	73	53,772	27	199,210
1956	224,173	133,436	66	68,618	34	202,054
1957	203,882	121,358	64	69,676	36	191,034
1958	213,842	127,287	60	85,394	40	212,681
1959	240,182	142,965	56	111,704	44	254,669
1960	249,452	148,483	55	119,138	45	267,622
1961	174,530	103,887	44	134,564	56	238,451
1962	190,450	119,874	44	151,408	56	271,282

TABLE VI

Chemical Composition of Meat of Atlantic Coast Oyster, British Oyster and New Zealand Oyster (83)

Constituents	Atlantic Oyster %	British Oyster %	New Zealand Oyster %
Water	86.0	76.84	75.2 - 78.8
Dry Matter	13.1		
Protein	6.2	11.18	12.20 - 13.72
Fat	1.2	1.97	1.83 - 3.66
Carbohydrates	3.7	8.0	
Glycogen		7.58	0.5 - 3.74
Sodium Chloride		0.22	
Other Mineral Substances		1.64	
Ash	2.0	2.02	

TABLE VII

Nutritive Values of Shrimp (83)

Food	g per 100 g			Calories per 100 g	mg per 100 g								
	Protein	Fat	Carbo-hydrates		Na	K	Ca	Mg	Fe	Cu	P	S	Cl
Shrimp	22.3	2.4	0.0	114	3840	404	320	105	1.8	0.80	270	340	5840
Shrimp (weighed with shells)	7.4	0.8	0.0	38	1260	133	105	35	0.6	0.26	89	112	1930

TABLE VIII

Nutritive Values of Oysters (34)

Food	g per 100 g			Calories per 100 g	mg per 100 g							
	Protein	Fat	Carbo-hydrates		Na	K	Ca	Mg	Fe	P	S	Cl
Oyster (raw)	10.2	0.9	Tr	50	505	258	186.0	41.8	6.0	267	249	815
Oyster (raw, weighed with shell)	1.2	0.1	Tr	6	61	31	22.3	5.0	0.7	32	30	98

III. THEORY AND METHODS OF QUICK FREEZING

Theory: The process which has given its name to "Quick Freezing" is the method of freezing all kinds of food very rapidly and although fast freezing may be the ultimate solution to all food preservation problems, it is nevertheless important.

In general, if foods are frozen very quickly, their quality upon thawing is better than if they are frozen slowly. Food contains water which is converted into tiny ice crystals during freezing and these crystals vary in size according to the speed of freezing. Slow freezing causes large crystals to develop, while more rapid freezing produces smaller crystals. In complex structures such as food which consists of a mixture of many complicated compounds and a great deal of water, there is no definite or fixed freezing point, and actual solidification takes place over a two or three degree temperature range. The strata in the temperature gradient is known as the "Zone of maximum crystal formation".

At first, it was postulated that the reason why quick frozen foods were better than foods frozen more slowly, was because when small ice crystals were formed during quick freezing, they would not burst or disrupt the tiny cells in the food, as would larger crystals, thus allowing the food nutrients to escape in the form of drip, after thawing (75). The reason for this trend of thinking was probably encouraged by the fact that much of the early work on fast freezing was done with meat, and there is absolutely no doubt that slow frozen meat is broken down

and does weep or drip more liberally than when quick frozen. This applies to most foods, and as an example, there is a difference between fast frozen and slow frozen strawberries when they are thawed and inspected immediately after freezing, and without long term storage. If, however, strawberries or other foods are stored for considerable periods after freezing, and before thawing and inspection, then the difference between those frozen quickly and those frozen slowly, becomes progressively less marked (74).

The advantages of fast freezing diminishes after storage, which indicates that fast freezing alone is not the answer to high grade frozen foods, and that conditions of storage are also important. It has been found that during storage, the small ice crystals formed during very rapid freezing tend to join together to form bigger ones, and eventually this original advantage of fast freezing is defeated (3). The joining together of small crystals to make larger ones can be reduced considerably if proper conditions of storage are assured. This requires storage at a lower temperature, coupled with absolute minimum variation of temperature above or below the mean prescribed. Every time frozen food rises a degree or two in temperature, and then drops again during storage, the joining together of ice crystals is accelerated and the quality of the food deteriorates.

More extensive research has shown that the actual size of the crystals formed within the frozen foods either at the time of freezing or as a result of storage conditions, insofar as large crystals might

burst open cells, is not strictly true. It is not a matter of big jagged crystals puncturing the cell and letting the juice out, but rather, it is a matter of where and how crystals are formed. As has been stated, foods are made of a complicated mixture of chemical compounds, some in the form of jelly-like substances (proteins), some either suspended or dissolved in water, but also attached to or forming a part of protein molecules (74). When the foods begin to freeze, three reactions occur (75).

(1) The free water begins to form with almost hard and almost pure lumps in the form of crystals, and in so doing throws out suspended solids which are dissolved in it.

(2) The water present in and forming in integral part of protein molecules forces its way out of them and again forms relatively pure crystals.

(3) In general, water contained within the main outer skin of the cell, tends to force itself out of the cell and form ice crystals on the outer side.

In order that any frozen food shall resume its original state, shape and size, after storage and thawing, the above described processes must be completely reverted. This can be achieved by proper processing of foods before freezing, by rapid freezing and proper storage.

Methods of Quick Freezing: Due to the great emphasis upon rapid freezing of foods, many inventors other than Clarence Birdseye have

devised various means of hastening freezing. Credit is to be given to Ottensen for perfecting the brine freezing of fish (78). R. B. Taylor invented a method of rapid freezing of strawberries and other fruits in invert sugar syrups (83). Zarotschenzeff (83) patented a process for freezing fish in brine fog.

Others who studied the freezing of foods by immersion in or spraying with sugar syrups included Bartlett and Woolrich (3) of the University of Texas.

Air Blast Freezing System: In the air blast freezing system, the foods to be frozen are placed upon racks or a moving belt within an insulated box and subjected to a blast of cold air. In this case, heat is removed from the food into the air and then transferred from the air to the cooling coils (79).

All blast freezers are basically the same and consists of a box containing a bank of cooling coils, and space for the foods to be frozen with fans to circulate the air over the product to the coils and back again. Special considerations must be given to blast freezer design and operation, as follows:

(1) The size of the compressor and cooling plant must be large enough to deal with the heat load imposed by the quantity of foods to be frozen and this will depend partly upon the specific and latent heat of each food.

(2) Since it is desirable to freeze the foods quickly and reduce them to a temperature of around 0°F, the operating temperature must be well below 0°F.

(3) All the heat extracted from the foods to cool and freeze them must pass to the cooling coils via the air. Therefore, enough air must be circulated to fulfill this function, and also, the foods must be arranged within the freezer so that air can circulate freely around them.

(4) Since there is always a tendency for moisture to migrate from a warm to a cold surface, steps must be taken to prevent the foods from becoming dehydrated during freezing.

In considering the above requirements, for heat flow from the foods to the air, and then from the air to cooling coils, there must be a series of "temperature gradient". That is the air must always be slightly colder than the foods, and the cooling coils must be slightly colder than the air. Thus, if the final temperature of the food is to be 0°F, then the air must be below 0°F, and the coils sufficiently below this temperature (79).

Air is capable of holding more or less suspended moisture according to its variation in temperature. The warmer the air, the more moisture it will hold. Therefore, if the warm air is cooled, there will approach a time the temperature drops, when the air can no longer retain all the moisture suspended in it. Continued cooling below this point will result in moisture being expelled from the air as dew or mist. It follows that if cold air comes into contact with warm foods and in so doing, itself become warmed, it will tend to pick up the moisture from the food. If that same air is then passed across the cold coils, it will deposit some of the moisture it formerly picked from the food, on to the coil.

So it is, that in a blast freezer, where air is constantly being warmed by food and then cooled again by pipes, moisture is constantly drawn from the food and passed to the coils, where it freezes as snow. This not only spoils the food and leads to a dried-out condition, but also it blocks up coils by filling spaces with snow and so reduces cooling capacity (83).

The dehydration of foods can be greatly reduced by the use of good packaging, but steps must be taken to prevent the undesirable effects of moisture migration during blast freezing. This can be achieved in either of the following procedures:

(1) Cooling may be staged, so that the product is relatively warm by keeping the temperature differences between the product to be frozen and the cold air.

(2) When no intermediate steps are employed, all the circulated air is kept at a much lower temperature than that actually required to remove the heat from the product and freeze it. In fact, air temperatures of about -30°F have been found to be ideal, because at such a low temperature, air is capable of carrying much moisture, and even though more air has to be circulated, the drying effect is reduced (11).

In all blast freezers, regardless of the type, it is advantageous to have large cooling coils operated at temperature required, rather than employing smaller coils at lower temperatures.

Multiple Freezers: Large quantities of food are frozen in multiple plate freezers. The original Birdseye freezer was called a double belt

froster and consisted of two long flexible steel belts, one superimposed above the other in an insulated tunnel. The packages containing food to be frozen were placed on the upper side of the lower belt. The lower side of the upper belt rested on the packaged products being frozen. Cold brine was sprayed down on the lower part of the upper belt and upon the upper part of the lower belt. This type of freezer is somewhat more flexible than the Birdseye freezer now used, in that packages of various thickness can be frozen simultaneously (4).

The modern type of plate freezers are suitable for freezing relatively thin packages. They resemble the original Birdseye belt frosters in that the product is frozen by placing it between two refrigerated metal surfaces which are called by a refrigerant. In present plate freezers, all of the packages placed on a single plate must be of uniform thickness. After loading, hydraulic pressure is applied to squeeze the packaged product between the refrigerated plates (2). In some freezers ammonia is circulated through sinous passages in the plates; in the others a freon refrigerant is used.

In general, plate freezers are quite satisfactory for freezing foods in relatively small packages of uniform thickness. They are unsuited for use when individually quick frozen products are desired, such as peas, whole kernel corn, aspargus stalks and the like.

Immersion Freezing by the Use of Cryogenic Gases: In recent years, several research and development laboratories have attempted to develop satisfactory means of freezing a number of products which have met the

usual quality standards of other frozen foods when frozen in air-blast and plate freezers. In some instances this has been accomplished by immersion freezing in liquid nitrogen or nitrous oxide (3).

The I. G. Farbenindustrie, of Frankfurt, Germany has been a leader in the study of immersion freezing in liquid nitrous oxide (79). Shortly after the termination of World War II, that company built a pilot plant having a capacity of one ton of food per hour, in which they studied the freezing of many kinds of vegetables and fruits. The nitrous oxide which boils off during the freezing operation is reliquified, and used repeatedly. Immersion in liquid nitrous oxide freezes small vegetables such as peas or lima beans, in a minute or two, whereas thirty minutes are required to produce individually quick frozen products on a belt in an air-blast freezer, and about two hours is required to freeze a ten-ounce package of these vegetables. Figure 3 shows the average freezing time by different methods.

A cut-up frying chicken (weight about 2 pounds) will freeze in 3 to 4 minutes by immersion freezing, during which time the sample immersed in 8°F, brine would not have begun to freeze, but merely be cooled to 20°F (5).

When whole strawberries are packaged and frozen by conventional processes, or individually frozen in an air-blast, the product is far from satisfactory. When frozen by direct immersion the product is far superior in its quality (5).

The thermal properties of liquid nitrogen and liquid nitrous oxide are presented in Table IX. These data are borrowed from 78, 4.

TABLE IX

Properties of Liquefied Gases for Immersion Freezing of Foods (78, 4)

	Nitrous Oxide	Nitrogen
Boiling Point (1 ATM, °F)	-127.237	-320.454
Latent Heat of Vaporization (at B.P., B.T.U./Lb)	161.78	85.67
Sensible Heat (Gas to 70°F) B.T.U./Lb	40.00	96.99
Total Heat to 70°F	201.78	182.66
Liquid Density at B.P. (Lb/Ft^3)	76.54	50.44
Gas Density at 0°C, ATM (Lb/Ft^3)	0.1148	0.078
Specific Volume, Standard Conditions (Ft^3/Lb)	8.711	13.80
Specific Heat Ratio (K) at 70°F, 1 ATM, $K = C_p/C_v$	1.260	1.40
Specific Heat, Constant Pressure at 70°F	0.2095	0.2484
Specific Heat, Constant Volume at 70°F	0.1609	0.1774
Molecular Weight	44.016	28.016
Color, Odor	None	None

IV. APPLICATION OF CRYOGENIC GASES FOR THE QUICK FREEZING OF FOODS

The word cryogenics means relating to cold, being derived from the Greek words 'kryos' which means 'icy cold' and 'genes' which means born. According to authorities (78) this word dates from about 1875, but apparently has not been used to any great extent before about 1955; prior to that date most authors used the term 'Low Temperature' to describe the research and applications of the science of cryogenics, which date back to about 1900 when the cryogenic gases were first introduced.

The average United States citizen consumes over 1,000 pounds of food per year. Of this amount, about 5 percent is handled as frozen food, 30 percent is handled without freezing but under refrigeration, and perhaps 1 percent is handled at room temperature and is protected from adverse environmental effects by shipment in an inert atmosphere. Each of these categories represents an application of cryogenics - the first two use liquid nitrogen as refrigerant, while the third belongs in the cryogenic group because the gaseous nitrogen required has been separated from the air by cryogenic means, in a manner similar to liquid nitrogen.

The dimensions of the volume of food handled under refrigeration in the United States alone can be judged from 1959 statistics (4). In that year, 8 billion pounds of frozen food, and 67 billion pounds of

perishable food were sold. The transport of this food required 115,000 railroad cars, 40,000 highway trailers, and 200,000 long and short haul trucks. Considering just the frozen food and assuming that 2 cubic feet of nitrogen would be required per pound of food transported from freezing plant to distributing warehouse, one can foresee a nitrogen demand of 16 billion cubic feet, or somewhat better than a billion pounds per year. Transport from the distributing warehouse to the retail marketer would increase this potential further. The use of liquid nitrogen for refrigeration of the fresh meat and produce which are shipped at 35°F, also would increase these figures.

The cryogenic gases are those gases whose boiling points are below -100°C (-148°F). Thus, they include most of the common atmospheric gases such as neon, krypton and xenon. Of other gases, the cryogenic group includes ethylene, which is a border line case, boiling at -104°C (-155°F). The four which are available in the greatest quantities, and which account for most of the cryogenic research and applications are oxygen, nitrogen helium and hydrogen. These four major crygenic gases may be classified into two groups, characterized as cold and very cold.

Nitrogen is the major constituent of air, accounting for 78 percent by volume or 75.44 percent by weight. Liquid nitrogen boils at -196°C (-321°F) and freezes at -210°C (-346°F). The thermal properties of liquid nitrogen are presented in the Appendix.

The volume of nitrogen produced is increasing, and is rapidly becoming a leader in chemicals produced in the largest quantity. There

are about 4 tons of nitrogen available in the air for every ton of oxygen. To day, about 0.5 tons of nitrogen per ton of oxygen is produced, the rest of the nitrogen being vented to the atmosphere. More air separation plants are being built every day, and a greater proportion of nitrogen to oxygen is being recovered as new uses of nitrogen develop and old ones expand.

In the United States alone, the production of elementary nitrogen in air separation plants today amounts to about 2.3 million tons per year (1).

The freezing of foods by liquid nitrogen is an attractive possibility, but not exactly a new one. Clarence Birdseye, reportedly tried it about 1925, but abandoned it because of the cost. The production of cheaper nitrogen and vastly improved insulation techniques are now leading to a re-examination of the commercial capabilities of this process. The freezing of foods by immersion in liquid nitrogen is primarily of interest for products that cannot be frozen satisfactorily by other methods.

An apparatus for immersion freezing of foodstuffs in liquid nitrogen is shown in Figure 1. It is a conveyor belt consisting of slats carried by two parallel chains. First contact with liquid nitrogen freezes all exposed surfaces, sealing in flavor and aroma. The process takes 7 minutes as compared to 15 to 60 minutes needed to freeze food by some conventional methods.

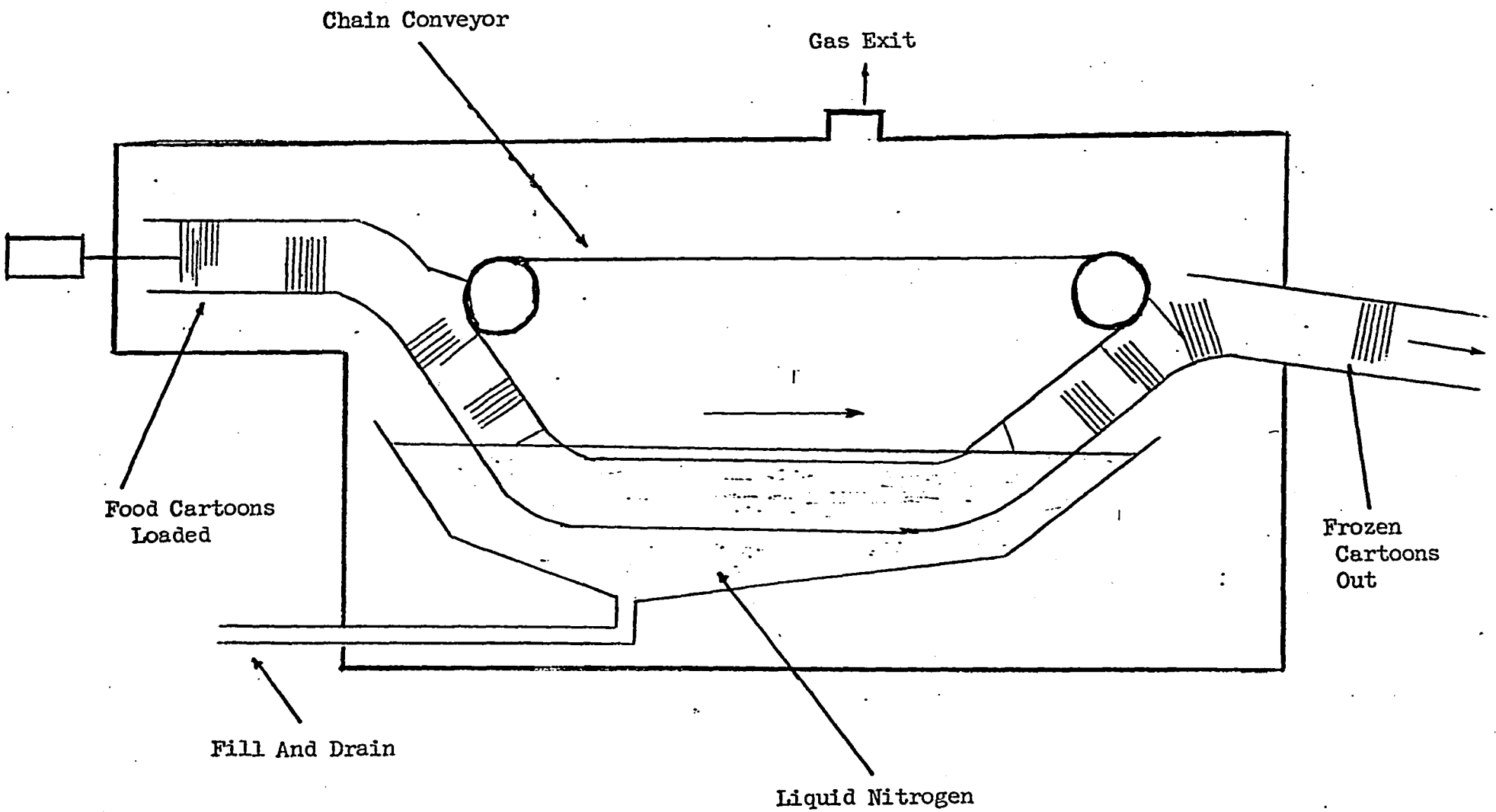


Figure 1 - Conveyor for Food Freezing by
Immersion in Liquid Nitrogen

In the liquidfreeze process, developed by Willard Morrison (76), liquid nitrogen is used to freeze the water content of food; and the process then relies on this ice, and the evaporation of the liquid nitrogen remaining in the insulated container to maintain food temperature at the required low level during shipment. In a six-week trip from California to New York via the Panama Canal, a mixed load of frozen food prepared by the liquifreeze process arrived at its destination at a temperature of -37°C (3).

In this process, liquid nitrogen is pumped into an insulated box packed with frozen food. As the liquid nitrogen vaporizes and escapes through vent holes in the box, the temperature drops to as low as -12 °C (-200°F). The temperature remains below zero for as long as a month.

In the Polarstream method, liquid nitrogen is stored aboard a truck or railroad car used to transport frozen foods. When the temperature falls to a predetermined level, a thermostat opens a valve on the liquid container and releases a stream of liquid nitrogen droplets and cold vapor through a manifold, located at the top of the refrigerated space. The cooling of the cargo space is rapid and effective.

The advantages of liquid nitrogen cooling as opposed to other mechanical methods of refrigeration can be summarized as follows:

(1) Liquid nitrogen cooling is simple to operate, the only moving part being the control valve, in the line from the nitrogen cylinder to the spray header.

(2) This method takes less precooling time, and nitrogen can cool at 0°F (-18°C) in less than 5 minutes. Figure 2 shows the cooling time of nitrogen immersion against conventional methods.

(3) It involves the use of automatic single valve control, combined with high cooling power to permit good control in hot weather and with frequent door openings.

(4) Liquid nitrogen in colorless, odorless, tasteless and non-toxic. It can be used in direct contact with foods without danger.

(5) Foods may be individually frozen in a very short time by direct immersion (Figure 3).

(6) The combination of low boiling point -196°C and the high heat of vaporization (86 B.T.U./lb) of liquid nitrogen, plus the fact that the gas absorbs about 80 B.T.U./lb in going from its boiling point to 0°F, makes liquid nitrogen an attractive cryogen.

(7) Nitrogen expands 600 fold in its transformation from a liquid to a gas. This cold gas constitutes an effective medium for cooling all parts of an enclosure.

There are already several companies using liquid nitrogen as a cryogen for food preservation. Companies using this process are Armour and Company (on meats), National Dairy Products (for research), Wilson and Company (on meats and poultry). Air Reduction Company and Air Products and Chemicals, Inc., also have similar nitrogen refrigeration systems in their research programs.

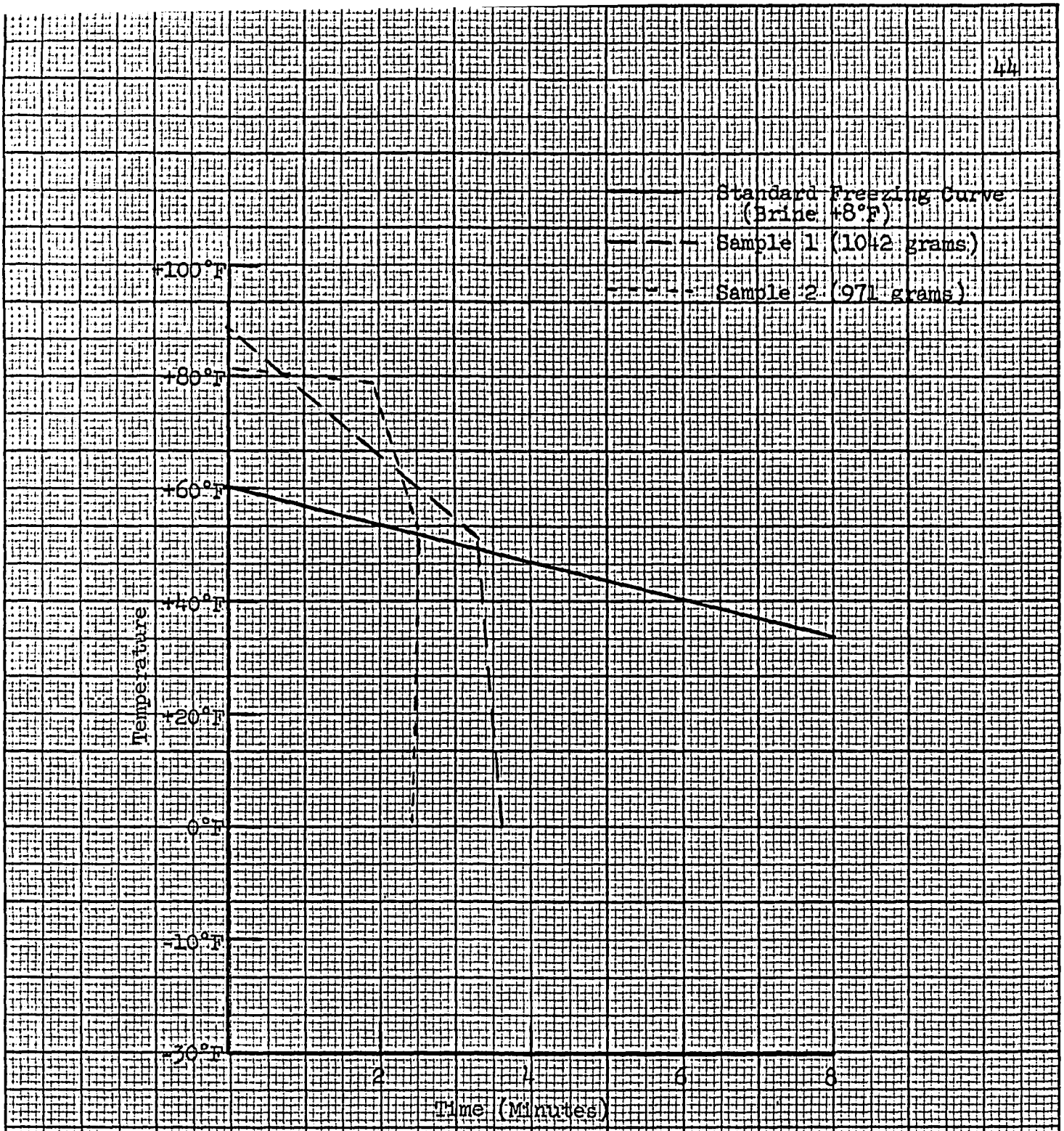


Figure 2 - Poultry Freezing Curves.
Nitrogen Immersion vs Standard Methods (50)

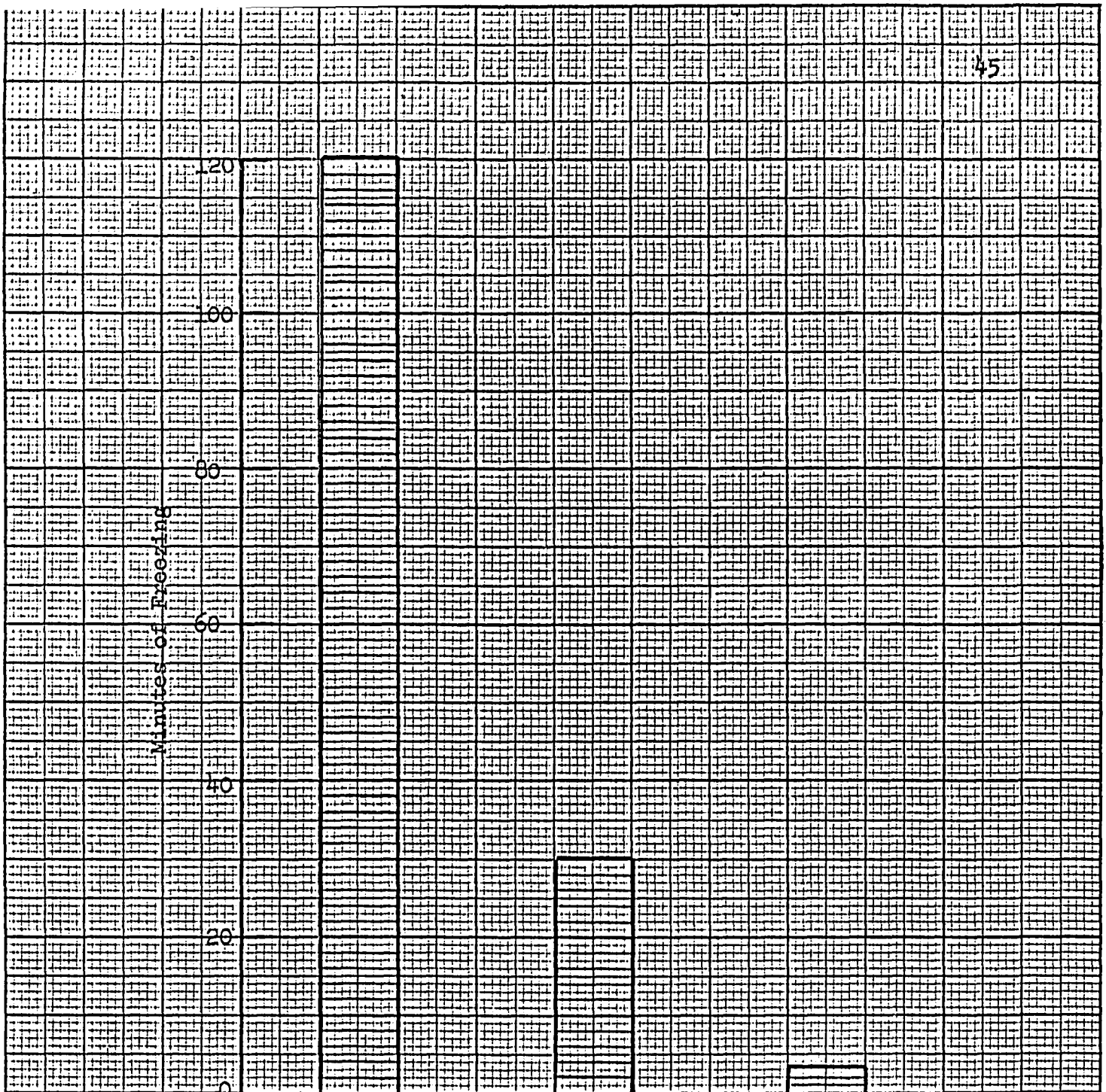


Figure 3 - Average Freezing Time by Different Method (3)

Tomatoes and bananas have been frozen by immersion in liquid nitrogen, and the products obtained are reported to retain many of the qualities of the fresh variety (78). An ear of corn frozen in this way can be divested of its kernels with no loss in nutrient content, flavor or kernel size (79). Strawberries and meats have been studied for the effect of immersion freezing in nitrogen, and even pastries and bakery goods have been frozen in this medium for commercial distribution.

A major break-through in the frozen food field - proof of the better quality obtained through immersion freezing in liquid nitrogen - has been achieved in the field of trial operations conducted by Air Reduction Company and a leading strawberry packer, G. A. Barem and Sons, of Beaverton, Oregon (3).

The drive for quality improvements by this method of freezing, led the Air Reduction Customer Service Laboratory, during its evaluation of the 'XYZ' factors of immersion freezing to apply these concepts to the freezing of strawberries. The Airco 'XYZ' factors are explained in Table XX.

During the test program, the cold-off gases (evolved gases) were utilized for three basis purposes:

(1) To provide refrigeration for removing heat prior to the actual freezing of the berries - "pre-cooling".

(2) To provide additional refrigeration for the frozen cartons of berries until such time as they were transported to the cold storage area - "post cooling".

(3) To provide additional refrigeration and controlled atmospheric conditions for the lugs of fresh product in storage areas - "supplementary refrigeration".

The obvious benefit from all three applications of cold gases was the extension of the storage period of fresh fruit to 72 hours or longer under the conditions provided by the cold storage nitrogen gas at 40°F. This can be compared to the normal procedures of 24 hours at 40-45°F, under mechanical means (4).

V. EXPERIMENTAL MATERIALS AND METHODS

Scope and Objectives of the Present Investigation

The objectives of the present investigation were to develop techniques for preserving oysters and shrimp which would employ liquid nitrogen as a cryogen. It was desired to obtain frozen shellfish which would retain its original flavor, texture, appearance, nutritive value and consumer acceptance.

It was then necessary to measure the specific heat of shellfish in order to determine accurately the volume of liquid nitrogen required to cool a given amount of shellfish to a given temperature. Knowledge of the specific heat is also required for calculating cooling and thawing time.

Preparation of Shellfish for Treating With Liquid Nitrogen

Shrimp: The shrimp used in the present investigation were caught in a net from a trawler. A 35 feet trawl net was used and the net was emptied on the deck of the boat. Along with the shrimp, all kinds of sea life were in the trawl. Trash fish, including small and broken shrimp were sorted out and discarded. The sorting operation was done as rapidly as possible after the net was emptied so that the shrimp could be washed and deheaded. The catch of approximately 60 pounds was divided equally into three parts and were stored in:

(1) crushed ice in the hold of the boat,

(2) a large stainless steel tank containing a three percent brine maintained at 28° to 32°F with liquid nitrogen, and

(3) in a large stainless steel tank maintained at 28° to 32°F in which shrimp were kept moist with a circulating spray of liquid nitrogen.

In another series of experiments, a catch of headed deveined shrimp of approximately 40 pounds was divided into two equal parts. The first half was rapidly frozen by immersion in liquid nitrogen (Figure 1), and the other half frozen by conventional methods. The product treated with liquid nitrogen was frozen in four minutes to a temperature of -10°F. Those frozen by conventional means were placed in a plate freezer at -20°F for eight hours. Both samples were packed and stored for a period of two, four and six months at 0°F.

Oysters: The oysters used in the present study were obtained from packing plants in the New Orleans area, Louisiana. The washed oysters of approximately 500 pounds were hauled in refrigerated trucks to the oyster house. They were unloaded in the shucking department, where they were shucked by professional shuckers. The oyster meat was thoroughly cleaned with fresh water according to F.D.A. regulations. Discolored meats, shell, etc., were discarded. They were then drained on a colander for five minutes. About 20 pounds of the cleaned oysters were stored in ice, and another 20 pounds of oysters were frozen in liquid nitrogen and packaged.

Samples were removed for initial chemical, bacteriological, histological and organoleptic studies at 0, 2, 4, 6, 8, 10, 12, 14 and 16 days. Frozen samples were withdrawn every two months for six months for similar tests.

Description of the Equipment

The equipment used for freezing shellfish by immersion in liquid nitrogen is as shown in the Figure 1. It is a conveyor consisting of slats carried by two parallel chains. The loaded food cartons enter from one end of the equipment and after being frozen by immersion in liquid nitrogen, they are brought out by the other end by the conveyor belt. Cartons of foods can be frozen continuously irrespective of the size of the food packages.

Determination of Specific Heat of Shellfish at Cryogenic Temperatures

Since liquid nitrogen was used during the present investigations to preserve shellfish, it was necessary to calculate the refrigeration load required to cool a given weight of shellfish to a desired final temperature. The specific heat values were also useful for calculating cooling and thawing time.

The apparatus used in the present experiment was essentially the same as the one used by Moline et al. (1957). The equipment is simple, the procedure is rapid and the results are accurate. A description of the apparatus is given in Figure 4.

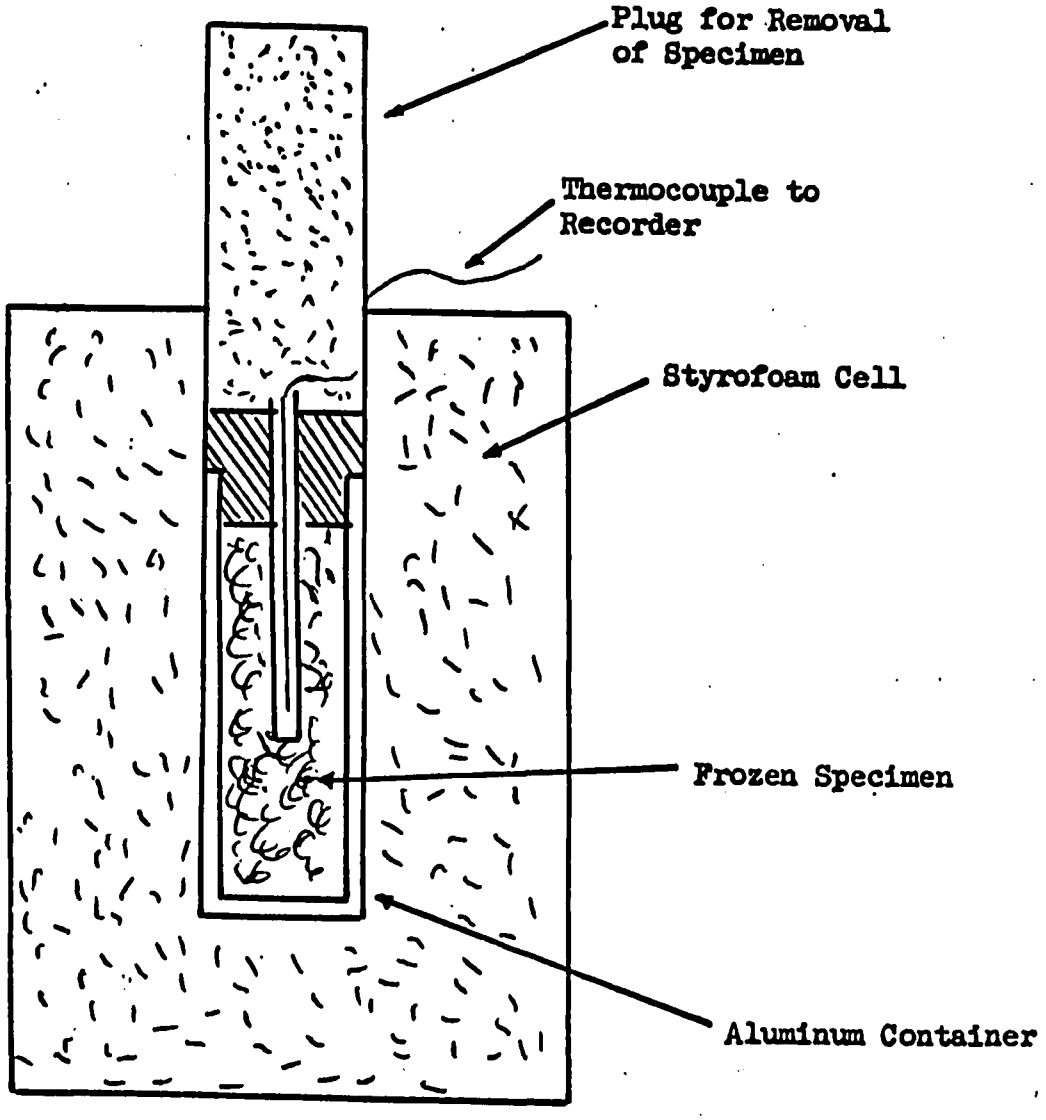


Figure 4 - Description of the Equipment for the Determination of the Specific Heat of Shellfish

It consisted of a rectangular block of polystyrene foam measuring 9.5 x 10.2 x 25.5 cm, the center of which had a cylindrical hole with a diameter of 1.4 cm and height equal to 20.3 cm. An aluminum sample container was placed in the hole. Care was taken to prevent rapid heat transfer to the sample by inserting a polystyrene plug at the top of the cell.

The apparatus was calibrated by using a specimen of known specific heat, since it was necessary to know the heat loss per unit area into the specimen during the slow warming period. For this purpose, a copper probe (ASRE) with a known specific heat and weight was used. The heat loss through the polystyrene foam into the copper probe was calculated by drawing a graph of time against temperature while cooling in liquid nitrogen.

The heat loss 'Q' was calculated from the following formula:

Q = (specific heat of copper) (weight of copper) (rate of temperature change)

where

Q = B.T.U.

Specific heat = B.T.U./lb °F

Weight = lb

Rate of temperature change = °F/minute (Δ T/t)

It was assumed that the heat loss into the cell was the same at any given temperature.

The specific heat of the shellfish was determined as follows: The specimen container was filled with a known weight of the sample and

cooled rapidly in liquid nitrogen (2-3 minutes). When the equilibrium temperature was attained, the container was removed and placed into the center hole of the polystyrene block. The block was maintained at the room temperature before the container was introduced into it. Temperature at the center of the sample was continuously measured with a copper-constantan thermocouple over the desired range. The rate of temperature change of the specimen container holding the material of unknown specific heat was measured. The specific heat of the specimen itself was calculated making use of the value 'Q'.

The specific heat of the entire specimen (C_{ps}) at a given temperature was equal to the heat loss (Q) divided by the rate of temperature change at that temperature and the weight of the specimen.

$$C_{ps} = \frac{Q}{[(\Delta T)/t](W_s)}$$

where

C_{ps} = the specific heat of the entire system (B.T.U./lb °F)

Q = heat loss through the polystyrene foam (B.T.U./min)

$\Delta T/t$ = rate of temperature change (degree/min)

W_s = weight of the entire system (lbs)

The specific heat of the unknown material was calculated by subtracting the heat capacity of the aluminum container ($C_{pa}W_a$) from the heat capacity of the unknown material plus container ($C_{ps}W_s$) and dividing this value by the weight of the unknown material (W_x).

$$C_{px} = \frac{C_{ps}W_s - C_{pa}W_a}{W_x}$$

where

W_x = weight of the unknown material (lb)

C_{px} = specific heat of the unknown material (B.T.U./lb °F)

C_{pa} = specific heat of aluminum (B.T.U./lb °F)

W_a = weight of the aluminum container (lb)

The change in specific heat values with temperature was determined by carrying out the above calculations for different temperatures.

Equations for Calculating Freezing and Thawing Times

Several investigators have given different formula for calculating freezing and thawing time. A solution for the calculation of the temperature distribution throughout a mass in which a change of state is occurring has been proposed by Neumann (59). The procedure is directly applicable to the calculation of freezing and thawing time under certain circumstances.

The equations expressing the temperature as a function of time and position in an infinite slab with a change of state as the material is being frozen are as follows:

$$v_1 = \frac{T_1}{\operatorname{erf}\lambda} \operatorname{erf} \frac{X}{2\left[\frac{K_1}{\rho_1 C_1}\theta\right]^{\frac{1}{2}}} \qquad (1)$$

$$v_2 = \frac{(V-T_1)}{\operatorname{erfc}\left[\frac{\frac{K_1}{\rho_1 C_1}}{\frac{K_2}{\rho_2 C_2}}\right]^{\frac{1}{2}}} \operatorname{erfc} \frac{X}{2\left[\frac{K_2}{\rho_2 C_2}\theta\right]^{\frac{1}{2}}} \qquad (2)$$

where

v_1 = temperature in frozen section

v_2 = temperature in thawed section

T_1 = temperature at which change of state occurs

K_1, ρ_1, C_1 = thermal conductivity, density, and specific heat of frozen material

K_2, ρ_2, C_2 = thermal conductivity, density and specific heat of thawed material

X = distance from surface of slab

θ = time

λ = factor determined from equation (3)

V = initial temperature of thawed material

erf = error function

erfc = coerror function

To determine the λ, equation (3) must be solved by trial and error.

$$\frac{e^{-\lambda/2}}{\text{erf}} - \frac{K_2\left[\frac{K_1}{\rho_1 C_1}\right]^{\frac{1}{2}}\left[V-T_1\right]\exp-\left[\frac{K_1}{\rho_1 C_1}\lambda^2/\frac{K_2}{\rho_2 C_2}\right]}{K_1\left[\frac{K_2}{\rho_2 C_2}\right]^{\frac{1}{2}} T_1 \text{erfc}\left[\lambda\left(\frac{K_1}{\rho_1 C_1}/\frac{K_2}{\rho_2 C_2}\right)^{\frac{1}{2}}\right]} = \frac{\lambda L \pi^{\frac{1}{2}}}{C_1 T_1} \qquad (3)$$

where L = latent heat.

The following assumptions are made while deriving these equations.

It is assumed that the surface comes to the temperature of the freezing medium immediately, and the surface temperature is at 0°F. If the surface temperature is other than zero on any temperature scale, a fictitious temperature scale must be employed so that in the fictitious

scale the surface temperature is at 0°. The above temperatures are applicable only for foods with high heat transfer coefficients.

A more simplified equation for calculating the freezing time is worked out below. The equation has the provision for the heat transfer coefficient, in calculating freezing time.

$$\theta = \frac{\lambda^1}{T_1}\left[\frac{Pd}{h} + \frac{Rd^2}{K}\right] \qquad (4)$$

where

θ = time for freezing to be completed

λ^1 = latent heat per unit volume

T^1 = the difference between the freezing time and temperature of the heating medium

h = heat transfer coefficient

K = thermal conductivity of frozen state

d = the diameter of sphere or cylinder, thickness of slab

P = 1/6 sphere, 1/4 cylinder, 1/6 slab

A modified version of Planks' basic equation was suggested by Nagaoka et al. (58) for the calculation of freezing time, which considered both the initial and final temperature. On the basis of this, the following equation for shellfish can be derived:

$$\theta = [1 + 0.0044\ (T_1 - T_2)]\left[\frac{Z}{V(T_2 - T_1)}\left(P\,\frac{d}{h} + \frac{Rd^2}{K}\right)\right] \qquad (5)$$

where

θ = freezing time

T_1 = initial temperature

T_2 = final temperature

T_4 = temperature of the medium

T_3 = final temperature of the frozen product

Z = heat to be removed from shellfish in lowering it from initial temperature to final temperature

V = specific volume of the ice, cu ft/lb

h = heat transfer coefficient

K = thermal conductivity of the frozen material

and the value of 'Z' was calculated from the following equation:

$$Z = C_w(T_1-T_2) + L_f + C_i(T_2-T_3) \qquad (6)$$

where

C_w = specific heat of shellfish above freezing

L_f = latent heat of fusion (B.T.U./lb)

C_i = specific heat of shellfish below freezing

Chemical Analysis of the Frozen Shellfish

The chemical analysis of the frozen shellfish included the determination of indole and trimethylamine nitrogen.

Indole: The indole content of each of the samples at different intervals of time was determined by Turner's method (13).

Twenty-five grams of the sample were weighed into a small beaker. The weighed portion of the sample was added to a quart-size Waring Blender bowl with 100 ml of 5% trichloroacetic acid and 25 ml of water,

and blended for 5 minutes at high speed. The contents of the bowl were transferred quantitatively to a 250 ml volumetric flask and diluted to volume with water. About 50 ml of this preparation were centrifuged at 2500 r.p.m. for 5 minutes. Twenty milliliters of the clear supernatant were transferred into a 250 ml separatory funnel. Ten milliliters of petroleum ether were added and the contents were shaken vigorously. The water layer was transferred to another 250 ml separatory funnel to which was added 10 ml of petroleum ether and the mixture was shaken. The petroleum ether fractions were combined in a separatory funnel. Ten milliliters of p-dimethylamino cinnamaldehyde reagent were added to the combined ether fractions and shaken vigorously. The colored aqueous layer was drained into a tube and centrifuged. Eight milliliters were pipetted into Klett tubes, the reagent added and allowed to stand for 30 minutes, after which time they were read in the Klett using a 640 mu filter No. 64. The concentration of the indole was expressed in micrograms of indole per 100 grams of the sample.

Trimethylamine Nitrogen: Trimethylamine nitrogen content of each sample was determined by a modification of the Dyer method (13). Twenty-five grams of the samples were weighed into a small beaker. The weighed portion of the sample was added to a quart-size Waring Blender bowl with 100 ml of 5% trichloroacetic acid and 25 ml of water and blended for two minutes at high speed. The contents of the bowl were transferred quantitatively to a 250 ml volumetric flask and made up to volume with water. About 50 ml of this preparation were centrifuged at 2500 r.p.m.

for 15 minutes. An aliquot of 1 to 4 ml of the clear supernatant was added to glass stoppered thiamine tubes and made up to 4 ml volume with water, 1 ml of 10% formaldehyde was added to each tube followed by 10 ml of toluene and 3 ml of a 50% potassium carbonate solution. The tubes were stoppered and shaken for 1 minute in a mechanical shaker. The lower aqueous layer was removed by suction with a glass tube drawn to a fine tip. The toluene layer was dried with anhydrous sodium sulfate. Five millliliters of the dried toluene portion were then added to "Spectronic 20" tubes containing 5 ml of 0.02% picric acid-toluene solution. The percent transmission of the yellow trimethylamine picrate, which developed, was determined with a "Spectronic 20" colorimeter at a wave length of 400 millimicrons. The concentration of the trimethylamine was expressed in mg of trimethylamine nitrogen per 100 grams of the sample.

Determination of Bacterial Counts of the Frozen Shellfish

Bacterial counts were made as explained in the Standard Method of Food Analysis using nutrient agar as the plating medium (82). The homoginate contained 100 grams of the sample in 500 ml of water and this was diluted 1:4 dilution for easy pipetting of the thick blended material.

A Quebec Colony counter was used for counting. The bacterial plate count was expressed as the number of colonies per gram of the sample.

Histological Studies of the Frozen Shellfish

The investigations carried out had the aim to determine the influence of the post-martem changes in animal tissues on its histological structures at freezing. The histological sections of the frozen tissues were prepared in the cold room. Fixation of the sections were performed in a 70 percent ethyl-alcohol, and then stained in hematoxyline.

Organoleptic Studies of the Frozen Shellfish

Organoleptic ratings were made on the basis of odor, appearance, texture and flavor. Sweetness was attributed for testing shrimp quality. Code of scores are as follows:

(10) No change from the fresh product of highest quality.

(8) First noticeable slight change in attributes.

(6) Moderate degree of changed attributes; increased in intensity and occurance from score of 8.

(4) Definite or strong degree of changed attribute.

(2) Extreme degree of changed attribute.

VI. RESULTS AND DISCUSSIONS

Specific Heat of Shellfish at Cryogenic Temperatures

With a method for measuring specific heat at low temperatures, it was possible to determine whether the specific heat of a complex system such as animal tissue was related to its composition. The specific heat was measured at low temperatures, and the values were compared with specific heats obtained by computation from the components, that is, from the specific heat of each component multiplied by its fractional concentration (Table X).

The computed values are consistently lower than the observed values by a factor of 1.11 ± 0.03. The possibilities of vitreous ice formation is suggested to explain the descrepancies between the observed and computed specific heat values for shellfish.

The correction factor for the computed specific heats of the shellfish measured is 1.09 ± 0.05.

Calculation of Liquid Nitrogen Consumption at Cryogenic Temperatures

Assumption

Basis: 1,000 lb/hr of shrimp (173,000 lb of shrimp per month)

Initial shrimp temperature	40°F
Final equilibrated temperature of glazed product	0°F
Glaze of 2 oz water per lb of shrimp meat, or 0.125 lb water per 1.0 lb of shrimp meat	
Glazing tank water temperature	33°F
Shrimp moisture content	83%

TABLE X

Specific Heat (C_p, B.T.U./lb °F) of Oyster and Shrimp

Temp. °F	-40	-30	-20	-10	0	10	20	30	40
ES[a]	.45	.45	.49	.55	.67	.89	1.71	.89	.88
EO[b]	.47	.48	.51	.52	.72	.89	.89	.89	.88
CS[c]	.44	.41	.46	.49	.54	.74	1.52	.72	.76
CO[d]	.45	.45	.45	.50	.62	.70	.70	.70	.71

[a] ES - experimental data for shrimp
[b] EO - experimental data for oysters

[c] CS - constituent analysis for shrimp
[d] CO - constituent analysis for oysters

Freezing point	28°F
Specific heat above freezing point	0.86
Specific heat below freezing point	0.45

Theoretical Refrigeration Available per Lb of Liquid Nitrogen

Temperature rise is from -320°F to +40°F

Latent heat, Q_1 = 86 B.T.U./lb

Sensible heat, Q_s = 0.25 (40 + 320) = 90 B.T.U./lb

Total heat absorbed, Q_t = 86 + 90 = 176 B.T.U./lb

Theoretical Refrigeration Required per Lb of Shrimp

Cool shrimp to 28°F	Q_1 = (1) (0.86) (40-28)	=	10.3 B.T.U.
Freeze shrimp at 28°F	Q_2 = (1) (0.83) (144)	=	119.6 "
Cool shrimp to 0°F	Q_3 = (1) (0.45) (28-0)	=	12.6 "
Cool glaze to 32°F	Q_4 = (0.125) (1.0) (33-32)	=	0.1 "
Freeze glaze at 32°F	Q_5 = (0.125) (144)	=	18.0 "
Cool glaze to 0°F	Q_6 = (0.125) (0.48) (32-0)	=	1.9 "

Total required refrigeration Q_t = 162.5 B.T.U.

Theoretical Liquid Nitrogen Consumption

C_t = 162.5/176 = 0.923 lb of liquid nitrogen/lb shrimp meat

System Losses and Efficiency Factors

a. Freezer efficiency is 80%; this includes such as:

heat leak through the freezer walls,
exfiltration of cold nitrogen gas,
infiltration of warm room air (maintained at minimum),
fan heat imput losses.

b. Storage tank filling losses are approximately 3% of the liquid nitrogen transferred (97% transfer efficiency).

c. Storage tank heat loss is equivalent to 0.5% per day loss based on full tank capacity. For a 7500-gallon tank the loss is 7500 lb of liquid nitrogen per month.

d. Transfer losses from storage tank to freezer (25 ft) are 375 B.T.U. per hour, which is equivalent to 2.13 lb liquid nitrogen per hour of operation. For one shift, 5 days per week operation, this loss is equal to 370 lb liquid nitrogen per month.

e. Freezer cleaning requires that the equipment be warmed and then cooled to operating temperatures once a day. This cool-down consumes approximately 4200 lb liquid nitrogen per month.

Calculated Liquid Nitrogen per Month

Theoretical liquid nitrogen consumption

(173,300 lb shrimp/month) (0.923 lb liquid nitrogen/lb shrimp)
= 160,000 lb liquid nitrogen/month

Actual liquid nitrogen consumption

$$\frac{\frac{370 + 160,000}{0.80} + 7550 + 4200}{} = 219,000 \text{ lb liquid nitrogen/month}$$

Actual liquid nitrogen consumption per lb shrimp

C_a = 219,000/173,300 = 1.26 lb of liquid nitrogen/lb shrimp

Summary of Liquid Nitrogen Consumption

Daily = 10,100 lb of liquid nitrogen (140,000 cf gas)

Monthly = 219,000 lb of liquid nitrogen (3,000,000 cf gas)

Chemical Analysis of the Frozen Shellfish

The results of indole and trimethylamine of the frozen shellfish are presented in Tables XI, XII, and XIII.

TABLE XI

Indole Content of Frozen Stored Oyster[a]

Age in Months	Indole Content (mcg/100 g)[b]	
	Conventional Refrigeration	Frozen in Liquid Nitrogen
0	0.72	0.72
2	1.14	1.06
4	4.08	2.85
6	6.93	4.76

[a]The values in the table above are the average of three samples; 20.0 g of each sample was taken out of a lot of 20.0 lbs of oyster.

[b]Indole content (mcg/100 g oyster):
2 = good quality
2-8 = insipient spoilage
8 = spoiled

TABLE XII

Indole Content of Stored Shrimp[a]

Age in Days	Indole Content (mcg/100 g)[b]		
	Iced Control	N_2 in Brine Immerson	N_2 + H_2O Spray
0	0.00	0.00	0.00
2	0.00	0.00	0.00
4	1.40	0.00	0.00
6	1.60	0.00	0.00
8	2.90	1.45	0.80
10	4.15	2.00	1.20
12	5.30	2.10	1.45
14	8.10	3.29	1.80
16	11.42	4.25	1.85

[a]Indole content (mcg/100 g shrimp)

2 = good
2-8 = insipient spoilage
8 = spoiled

[b]The values in the table above are the average of three samples: 20.0 g of each sample were taken out of a lot of 20.00 lbs.

TABLE XIII

Trimethylamine Content of Stored Shrimp[a]
After Various Treatments

Age in Days	Trimethylamine N_2 (mg/100 g)[b]		
	Iced Control	N_2 in Brine Immersion	$N_2 + H_2O$ Spray
0	0.00	0.00	0.00
2	0.00	0.00	0.00
4	0.01	0.00	0.00
6	0.20	0.00	0.00
8	0.35	0.00	0.00
10	0.61	0.15	0.00
12	1.20	0.27	0.15
14	1.32	0.36	0.21
16	1.40	0.70	0.47

[a]The values in the table above are the average of three samples; 20 g of each sample was taken out of a lot of 20.0 lbs.

[b]When headless shrimp are stored in direct contact with ice a trimethylamine nitrogen value of 1.5 mg per 100 g shrimp or higher is a definite indication of spoilage.

No simple and dependable tests for shellfish quality are presently available. Extreme biological differences, seasonal variations, and use of the whole organisms in the tests complicate the analytical problems. Need for a measure of shellfish quality long recognized by industry and public health officials, has prompted numerous investigations. Most of this reasearch has failed to fulfill the need, but tests for indole and trimethylamine nitrogen have recently been proposed as possible spoilage indicies for shellfish. The spoilage is caused by the liberation of these compounds through the action of microorganisms. From a determination of indole and trimethylamine in a frozen sample, it should be possible, to arrive at a numerical quality index. From such data it would be possible to state the length of time the product had been stored, its probable future storage life, whether adequate and correct method of refrigeration was utilized for freezing the sample, and its quality at any given instant (22).

It was observed by experimental results, that the shellfish frozen by conventional refrigeration had a higher indole and trimethylamine nitrogen content compared to the samples cooled by liquid nitrogen, at the end of each test period. In addition to this fact, the rate of formation of these compounds was more rapid in the ice stored controls than the samples cooled by liquid nitrogen.

Total Bacterial Counts of the Frozen Shellfish

The total bacterial counts were less in the shellfish samples frozen by liquid nitrogen compared to ice control at the end of each test period.

Bacteria and moulds do not cause any trouble during the low temperature freezing and storage stages, as these organisms are rendered dormant at low temperatures and therefore do not continue to multiply (83). A large percentage of the bacteria contained in shellfish were killed during rapid freezing by liquid nitrogen and these values are indicated in tables. XIV, XV.

Histological Studies of the Frozen Shellfish

Histological studies showed that the product frozen rapidly developed smaller crystals, and less protein concentration than the shellfish frozen by mechanical refrigeration. The state of the histological structure also influences the consistency and appearances of the muscular tissue. The histological characteristics are connected with the capacity of the tissue to re-absorb the muscular juice during thawing. However, it should be noted that all investigations concerning histological changes occurring at freezing refer to one aspect of the problem. It is the dependence of size of, and number of ice crystals on the freezing rate.

The experiments performed in our laboratories were designed to observe the histological structure at freezing.

Smaller ice crystal formation and less concentration of the protein resulted in less drip loss upon thawing of the product frozen in liquid

TABLE XIV

Bacterial Count on Frozen Stored Oyster

Age in Months	Bacterial Count, Colonies/g[a]	
	Conventional Refrigeration	Frozen in Liquid Nitrogen
0	25,000	21,000
2	22,000	17,000
4	36,000	18,000
6	20,000	11,000

[a]Counts in excess of 1 million indicate the onset of spoilage.

TABLE XV

Bacterial Counts on Stored Shrimp
After Various Treatments

Age in Days	Bacterial Counts Colonies/g x 10^3		
	Iced Control	N_2 in Brine Immersion	$N_2 + H_2O$ Spray
0	7	7	7
2	185	80	100
4	420	154	180
6	950	290	340
8	2,200	510	600
10	5,100[a]	960	1,100
12	9,200	2,100	2,150
14	16,500	4,700	3,500
16	24,300	9,100	5,450

[a]Counts in excess of 5 million indicate the onset of spoilage.

nitrogen. Figures 5 and 6 illustrate the histological structure of the shrimp frozen by conventional refrigeration and by liquid nitrogen.

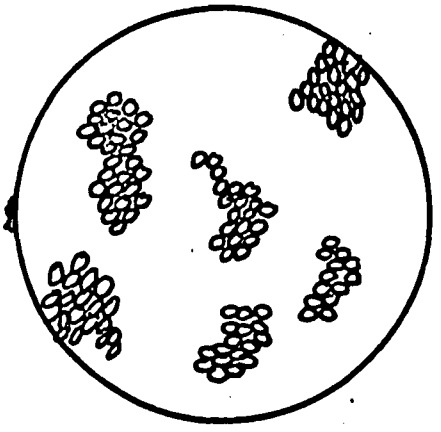
Organoleptic Ratings on the Frozen Shellfish

The results of the organoleptic studies are presented in Tables XVI, XVII and XVIII.

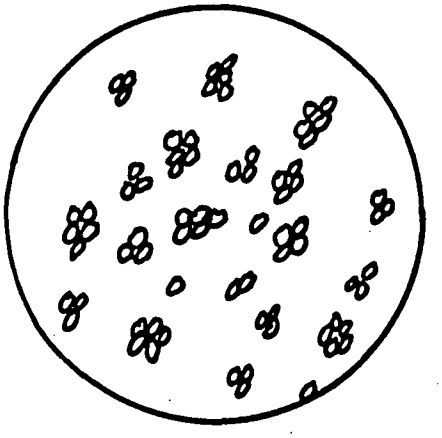
Organoleptic ratings in each test are the averages of at least 100 individuals who had a professional knowledge of judging the changes in shellfish odor, flavor, texture and appearance.

Economics of Using Liquid Nitrogen as a Cryogen for the Preservation of Foods

At present, the cost of freezing with liquid nitrogen per pound of raw material varies between 7.5 cents to 9.0 cents, compared to 6 cents per pound by conventional freezing methods. Comparative costs of foods freezing by various processes are presented in Table XIX. However, more efficient methods of producing liquid nitrogen are reported by several research and development departments of various food industries (3). It has been reported by these organizations that it is possible to reduce the cost of liquid nitrogen by several cents per pound, making the cost of liquid nitrogen food freezing less than 7 cents per pound. This would bring liquid nitrogen within 20 percent of being competitive to other methods of refrigeration. Its unique advantages make possible certain other savings and improved quality either of which could make it competitive. (Table XX)

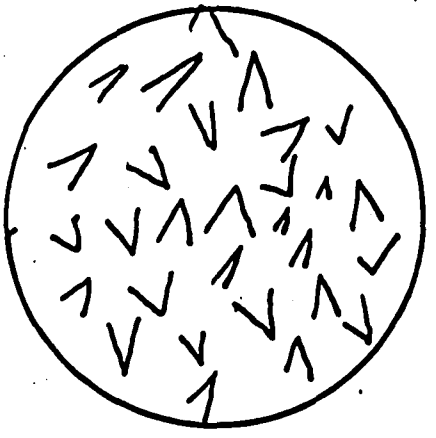


(a) Conventional refrigeration (protein concentration was observed)

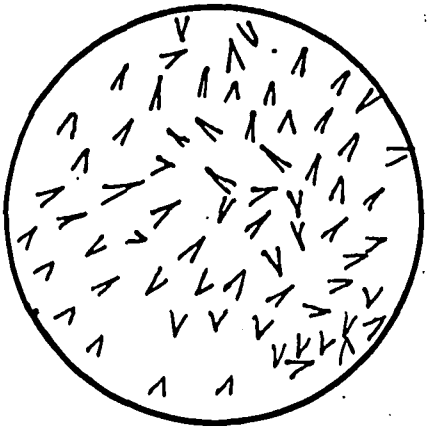


(b) Liquid nitrogen freezing (protein was more uniformly distributed)

Figure 5 - Illustration Showing the Protein Distribution When Shrimp was Frozen by Two Different Methods



(a) Conventional refrigeration (occurrence of big ice crystals were noticed)



(b) Liquid nitrogen freezing (occurrence of small ice crystals were noticed

Figure 6 - Illustration Showing the Formation of Ice Crystals When Shrimp Were Frozen by Two Different Methods

TABLE XVI

Organoleptic Scores on Stored Shrimp
After Various Treatments

Age in Days	Organoleptic Score		
	Iced Control	N_2 in Brine Immersion	$N_2 + H_2O$ Spray
0	9.7[a]	9.7	9.7
6	8.2	8.5	8.6
12	6.3	7.7	7.5
16	3.9	6.4	6.1

Organoleptic ratings are averages of 125 individuals, and are based on odor, appearance, sweetness, flavor and texture.

[a]CODE OF SCORES:

(10) No change from the fresh product of highest quality.
(8) First noticeable slight change in attributes.
(6) Moderate degree of changed attribute: increased in intensity and occurrence from score of 8.
(4) Definite or strong degree of changed attribute.
(2) Extreme degree of changed attribute.

TABLE XVII

Organoleptic Scores on Frozen Oyster

Age in Months	Average Organoleptic Score[a]	
	Conventional Freeze	Frozen in Liquid Nitrogen
0	9.5	9.5
2	7.9	8.4
4	6.4	7.5
6	4.2	6.1

Organoleptic ratings are average of 116 individuals, and are based on odor, flavor, texture and appearance.

[a]CODE OF SCORES:

(10) No change from the fresh product of highest quality.
(8) First noticeable slight change in attributes.
(6) Moderate degree of changed attribute: increase in intensity and occurrence from score of 8.
(4) Definite or strong degree of changed attribute.
(2) Extreme degree of changed attribute.

TABLE XVIII

Organoleptic Scores on Frozen Shrimp

Age In Months	Organoleptic Score	
	Conventional Freeze	Frozen in Liquid Nitrogen
0	9.4	9.4
2	7.5	8.5
4	5.2	7.6
6	3.1	5.3

Organoleptic ratings are averages of 104 individuals, and are based on odor, appearance, sweetness, flavor and texture.

CODE OF SCORES:

(10) No change from the fresh product of highest quality.
(8) First noticeable slight change in attributes.
(6) Moderate degree of changed attribute: increased in intensity and occurrence from score of 8.
(4) Definite or strong degree of changed attribute.
(2) Extreme degree of changed attribute.

Another method of reducing the cost of liquid nitrogen is that of installing an on-site liquefying system. Depending on the power costs, it looks as though on-site production of liquid nitrogen could make the nitrogen system directly competitive with conventional refrigeration systems such as contact plates. For the actual freezing process excluding all but capital and energy costs, an approximate calculation yields a cost of 1.3 cents per pound of raw product for liquid nitrogen freezing compared to 1.25 cents by contact plate freezers. One advantage of liquid nitrogen system is in the cost of buildings. It is a high capacity system and can accomplish in 1,200 square feet the same capacity as a plate freezer would require in 10,000 square feet to do. In addition, construction costs per square foot can be about one-half of those needed in conventional processes. This will result in a high reduction of initial capital requirements.

A high percentage of the present cost of liquid nitrogen presently marketed involves the distribution and handling costs. With growing demands for liquid nitrogen and with the improved methods of producing liquid nitrogen, it is possible to reduce not only the production costs but also the distribution and handling costs. Figure 7 illustrate the high purity nitrogen demand for the coming years. With the increasing use of oxygen in steel making, nitrogen may become more available since, for every pound of liquid oxygen obtained, four pounds of liquid nitrogen could be obtained with a relatively small additional cost. If the steel companies begin to consider nitrogen as a lucrative

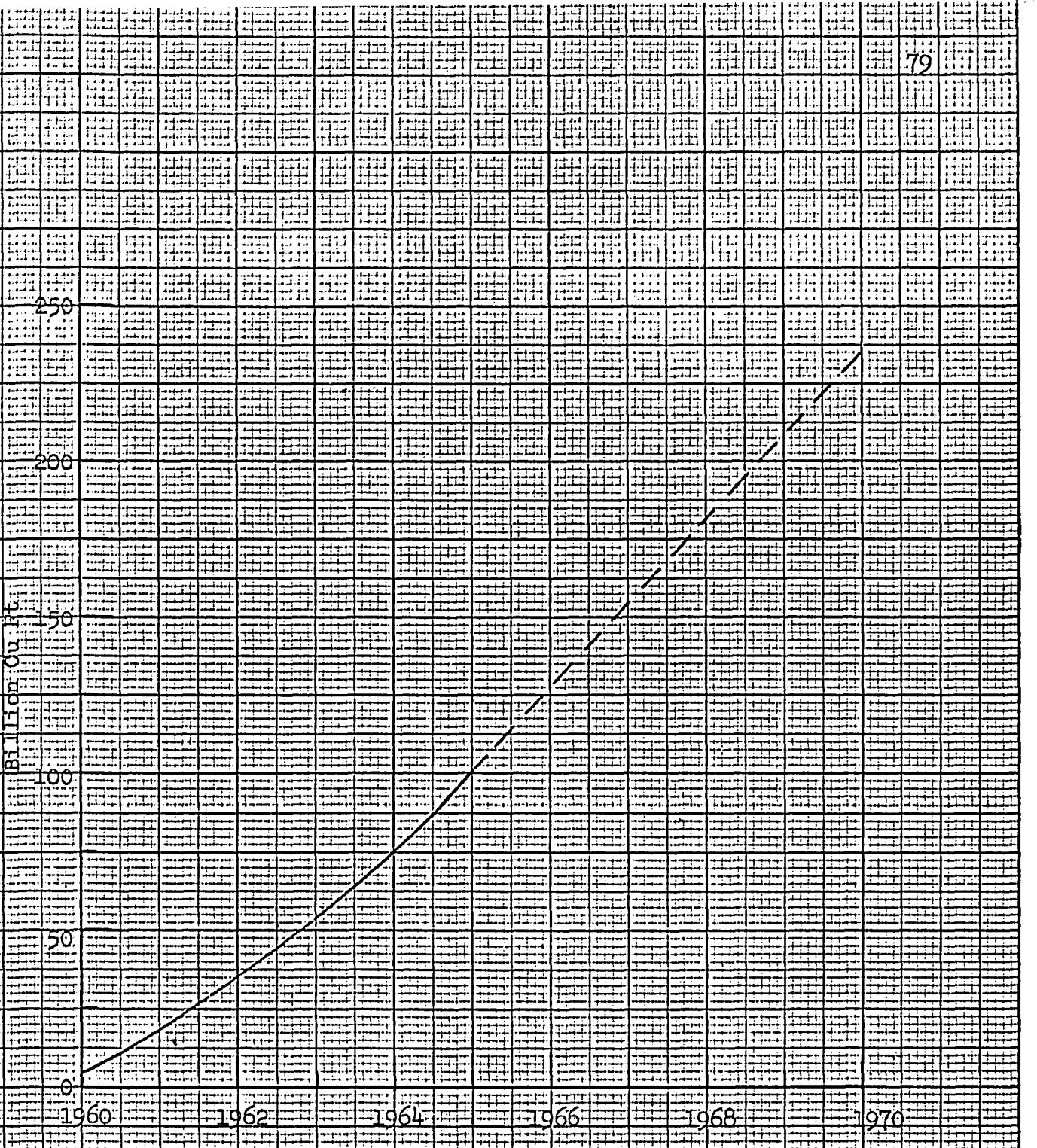


Figure 7. - Increasing High-Purity Nitrogen Demand in the United States (1)

TABLE XIX

Comparative Costs of Foods Processing

Process Used	Present Processing Cost Per Pound of Raw Product[a]
Freeze Drying	13.8 cents
Liquid Nitrogen Freezing (with liquid nitrogen at 3 cent/lb)	8.7 "
Standard Freezing	5.8 "
Irradiation Sterlization	4.1 "
Dehydrofreezing	3.3 "
Standard or Aseptic Thermal Treatment	2.9 "
Spray Drying	1.6 "
Foam Mat Drying	1.6 "
Drum Drying	1.2 "

[a]Assumes raw product 20 percent solids, 100 ton per day capacity, 5 months processing season. Includes energy costs and transportation costs from West Coast to Eastern Centers. Costs exclude payment for raw materials, packaging material, handling, installation and buildings.

by-product, they may begin to insist on this added capability being a part of the new liquefying systems in the near future.

The liquid nitrogen process appears to be most attractive for non-seasonal use where its characteristics of continuous flow can be used to greatest advantage and where change over from one product to another does not disrupt the processing line greatly. It is technically attractive as a first phase process for items which are intended for the freeze drying process. It is space saving, can be used at low capacities and does not need to be matched with a cold storage. It may also prove to be an attractive adjunct to existing conventional plants as a simple expedient method of handling seasonal surges of production, thus reducing waste and allowing more rapid processing of incoming raw materials.

Liquid nitrogen freezing might easily compete with other freezing methods, but this depends on reducing production costs.

VII. SUMMARY

Liquid nitrogen has been successfully used for the preservation of shellfish (shrimp and oysters). Cooling and freezing with liquid nitrogen did not produce undesirable changes in the products. Chemical, bacteriological, histological and organoleptic tests showed that the shellfish stored in liquid nitrogen were superior to ice stored controls and retained their original nutritional qualities. The shellfish of the cryogen frozen shellfish was extended several folds.

Specific heat of shellfish was measured to determine accurately the volume of liquid nitrogen to cool a given amount of shellfish to a given temperature. The specific heat is also required for calculating cooling and thawing time.

The freezing of food stuffs by liquid nitrogen is an attractive possibility. The combination of the low boiling point -320°F and the high heat of vaporization (86 B.T.U./lb) in going from its boiling point to 0°F makes liquid nitrogen an efficient refrigerant. A further advantage is the fact that the nitrogen expands 600-folds in its transformation from a liquid to a gas, this cold constituting an effective medium for cooling all parts of an enclosure.

TABLE XX

The 'XYZ' of Immersion Freezing (3)

'X' for Extra Quality	'Y' for Yield	'Z' for Exotic New Products
Texture	Rapid throuput	Whole kernel corn
Flavor	Great flexibility	Tomatoes
Color	Low equipment cost	Citrous cells
Aroma	Space saving	Avacadoes
Appearance		Fruit and vegetable powders
Vitamin Retention		
Drainage (Cell Damage)		
Shelf Life		

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APPENDIX

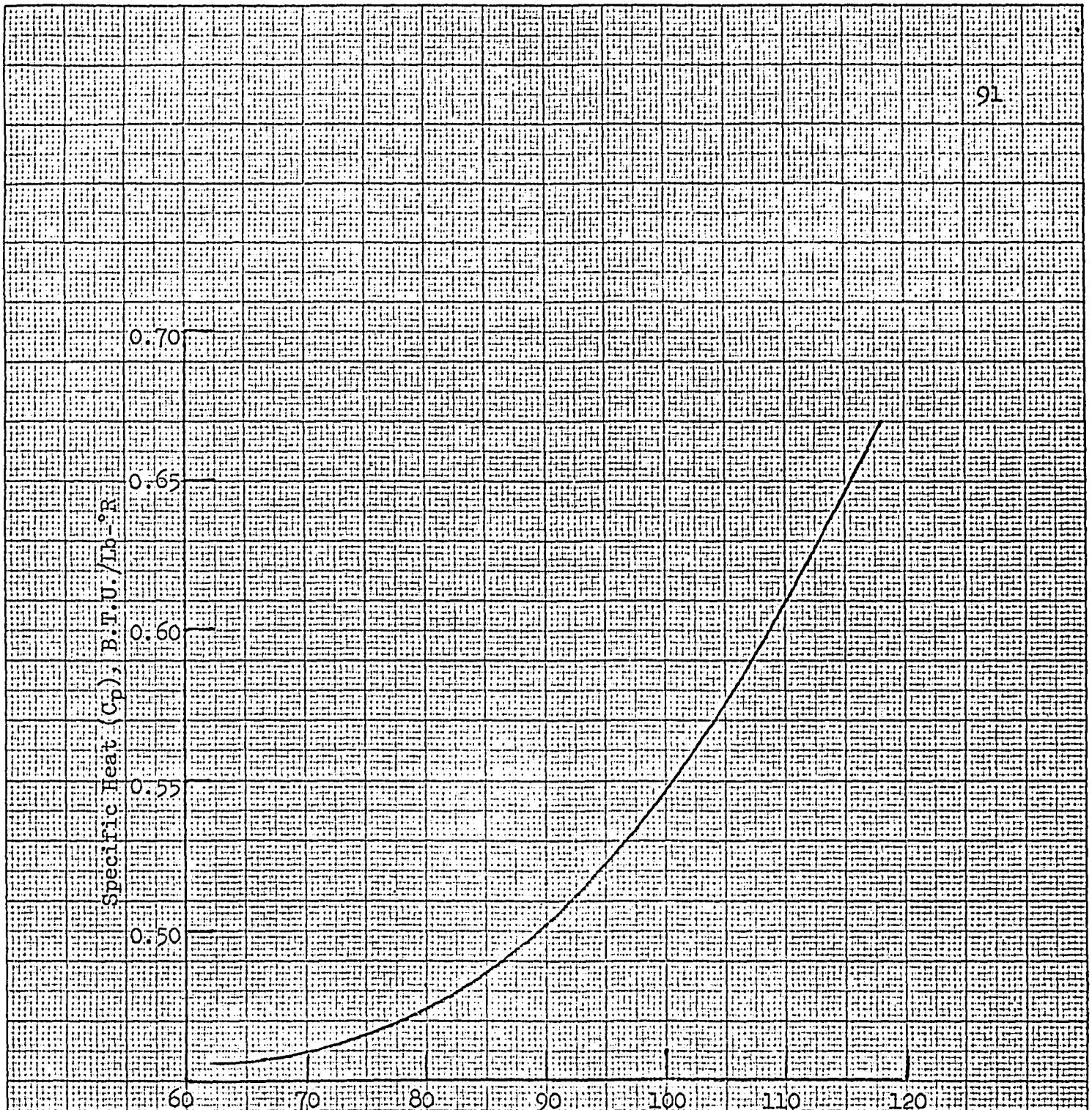

Figure 1a - Specific Heat (C_p) of Saturated Liquid Nitrogen (28)

Specific Heat (C_p) of Liquid Nitrogen (28)

Temperature °K	C_p cal/gm-mole-°K	Temperature °K	C_p cal/gm-mole-°K
63.95	13.34	79.17	13.76
65.02	13.33	82.64	13.95
66.9	13.54	89.50	14.16
68.4	13.64	95.39	14.50
68.41	13.45	95.46	14.71
69.15	13.40	99.55	15.04
70.2	13.63	103.31	15.63
70.28	13.45	103.72	15.56
71.8	13.66	107.72	15.99
72.69	13.56	107.48	16.10
73.5	13.69	111.57	17.30
74.57	13.59	112.97	17.60
75.46	13.74	115.25	18.27
76.58	13.68	116.99	18.72
77.74	13.64		

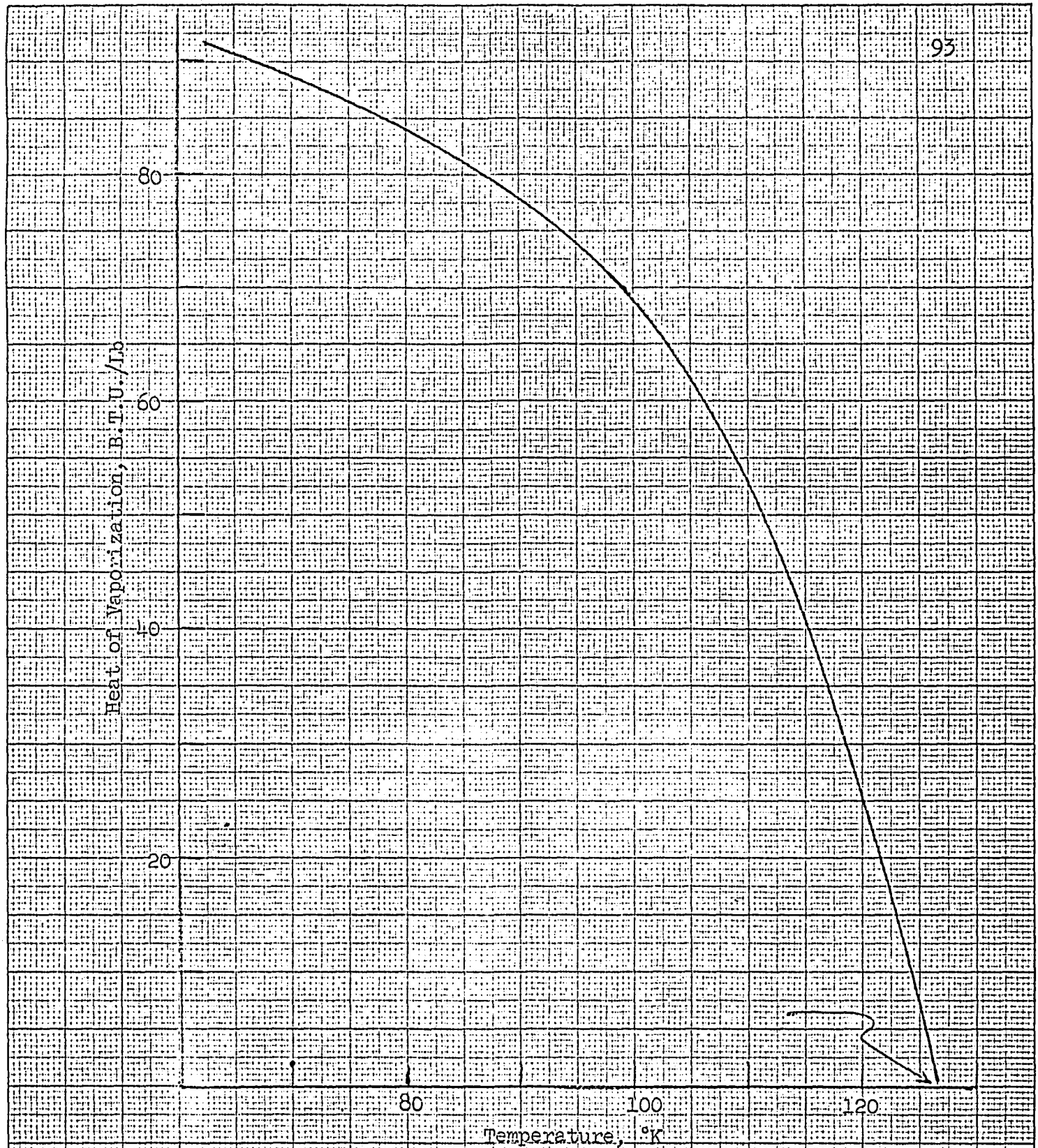

Figure 2a - Heat of Vaporization of Nitrogen (25, 55)

Heat of Vaporization of Nitrogen (25, 55)

	Temperature °K	Heat of Vaporization, ΔH_v joules/mole	cal/mole
Solid	62.00	6775.0	
	62.0018	6787.4	
	62.0172	6762.4	
	67.9588	5901.6	
	67.9620	5899.0	
	68.00	5899.0	
	73.0913	5739.1	
	73.0887	5732.1	
	73.10	5735.2	
	77.395	5592.2	
	78.00	5579.4	
	78.0147	5563.1	
	78.0153	5571.8	
Liquid	80		1313
	85		1266
	90		1213
	95		1155
	100		1086
	105		1010
	110		918
	115		803
	120		643
	125		328
	126.1*		

*Critical point

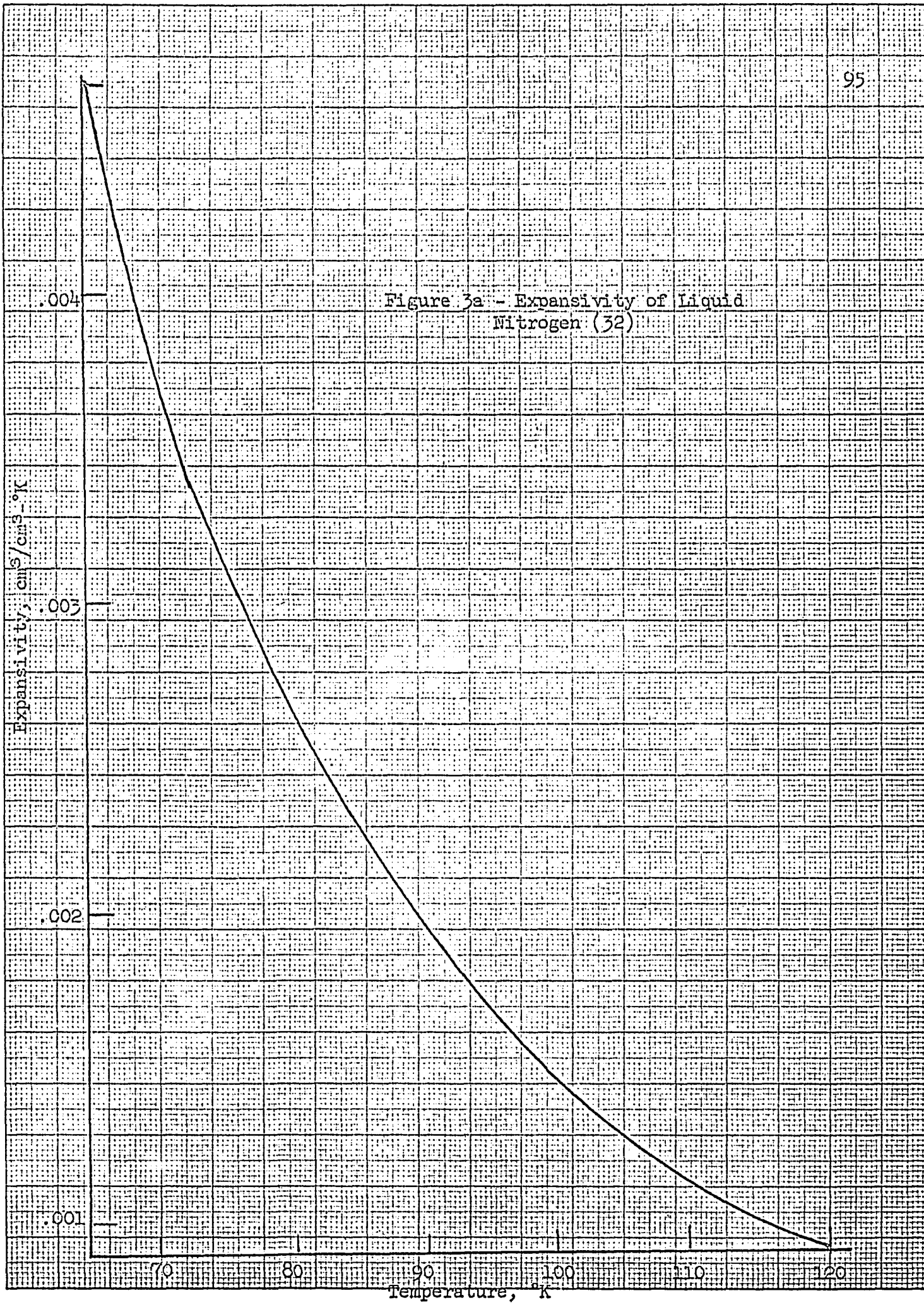

Figure 3a - Expansivity of Liquid Nitrogen (32)

Expansivity of Liquid Nitrogen (32)

Pressure		Temperature	βL
kg/cm^2	atm	°K	1/°K
1	0.968	63.14	
79.0	76.459	64.84	0.004 56
202.0	195.50	67.40	.004 14
354.7	343.29	70.46	.003 49
504.1	487.89	73.36	.003 17
710.9	688.04	77.24	.002 92
1066.8	1032.5	83.57	.002 39
1422.7	1376.9	89.54	.002 03
1920.7	1858.9	97.40	.001 68
2631.9	2547.3	107.83	.001 07
3555.6	3441.3	120.29	.000 94

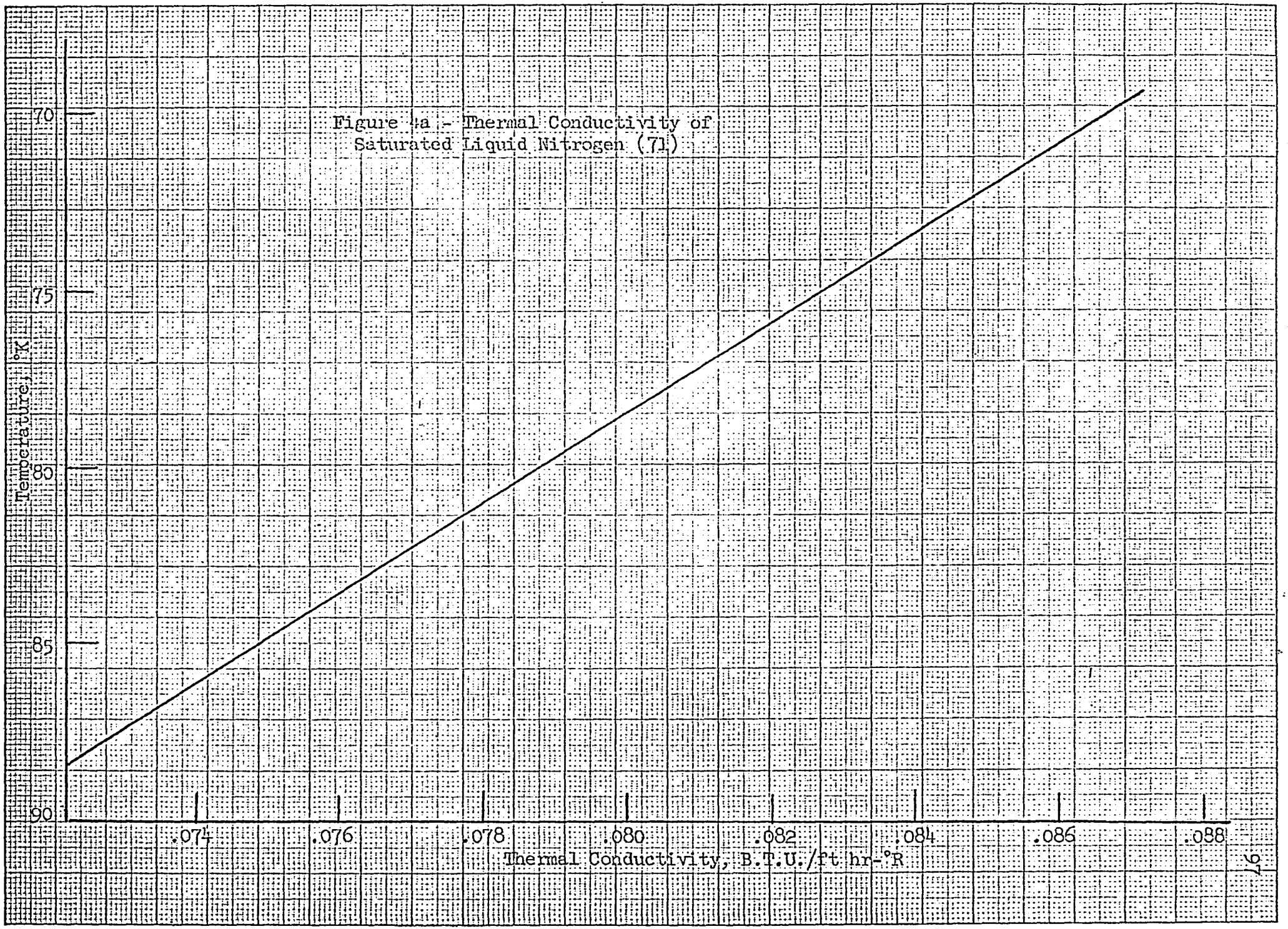

Figure 4a - Thermal Conductivity of Saturated Liquid Nitrogen (71)

Thermal Condustivity of Liquid Nitrogen (71)

Temperature °K	Thermal Conductivity cal/cm-sec-°K
68.68	3.64×10^{-4}
69.92	3.53 "
70.94	3.59 "
73.66	3.44 "
76.26	3.39 "
77.66	3.33 "
78.73	3.31 "
81.11	3.18 "
81.77	3.15 "
83.77	3.12 "
86.44	3.07 "
88.12	3.00 "

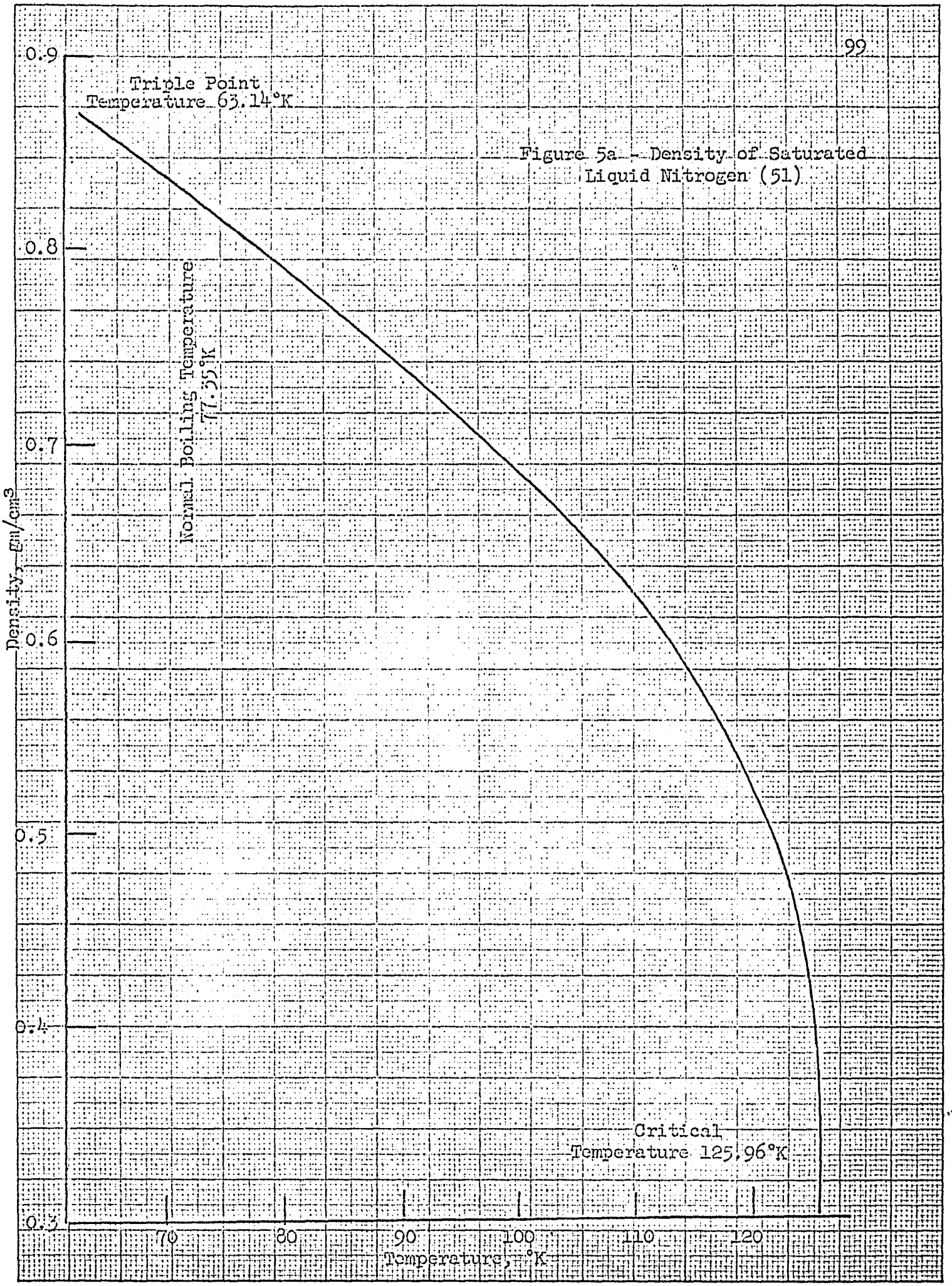

Figure 5a - Density of Saturated Liquid Nitrogen (51)

Density of Liquid Nitrogen
(Saturated) (51)

Temperature °K	Density gm/cm³
63.14+	
64.73	0.8622
77.31	.8084
77.32‡	
77.5	
78.00	.8043
90.58	.7433
99.36	.6922
111.89	.6071
119.44	.5332
125.01	.4314
125.96*	.31096

*Critical Temperature
+Triple Point Temperature
‡Normal Boiling Temperature

VITA

Ramachandra M. R. Rao was born in Bangalore, India on October 30, 1931. He received his elementary and high school education at Bangalore. He graduated in 1959 from Central College, Bangalore, University of Mysore with a Bachelor of Science degree.

In March, 1960, he came to the United States to study in chemical engineering and attended the University of Houston. He obtained his Bachelors degree in Chemical Engineering in August, 1962. In September, 1962, he enrolled at the Louisiana State University as a graduate student in the Department of Chemical Engineering, where he received his Masters degree in Chemical Engineering in August, 1963. He was awarded a United States Atomic Energy Commission Research Assistantship throughout his graduate work. He is presently a candidate for the degree of Doctor of Philosophy in Food Science and Technology.

EXAMINATION AND THESIS REPORT

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Major Field: Food Science and Technology

Title of Thesis: Thermal Properties of Cryogen Frozen Foods and Changes Occurring at Sub-zero Temperatures

Approved:

Arthur F. Novak
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

December 15, 1965